RECOVERY OF POLY (ETHYLENE TEREPHTHALATE) FROM USED X-RAY FILM

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C O N T E N T S

A C K N O W L E D G E M E N T S

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I am especially grateful to my wife, Nerina, for her constant encouragement throughout the years of this work.

D E C L A R A T I O N

This is to certify that neither this thesis, nor any part of it, has been presented or is being concurrently submitted in candidature for any other degrees.

CANDIDATE 

DATE ..15th December 1992.....

C E R T I F I C A T E O F R E S E A R C H

This is to certify that, except where specific reference is made, the work in this thesis is the result of the investigation carried out by the candidate.

CANDIDATE 

DIRECTOR OF STUDIES 

DATE .15th December 1992.....

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The thesis describes experimental work to remove primary contaminants viz silver and poly (vinylidene)chloride (PVDC) coating, from X-ray film and subsequent recovery of poly (ethylene) terephthalate (PET) economically.

The thesis commences with a review of the literature, concerning the recycling and recovery of (PET), from X-ray films and related materials.

Following a discussion of the properties of (PVDC) and PET, a programme of experimental work is outlined, for de-silvering the X-ray film, removal of PVDC and recovery of PET.

From a consideration of the preferred experimental procedure, an estimated materials and process costing is outlined, for a proposed PET recycling plant.

Management and recycling, within the EC, specifically in relation to the recovery of PET, is discussed, particularly in relation to the legal restraints on the disposal of plastics to land-fill sites.

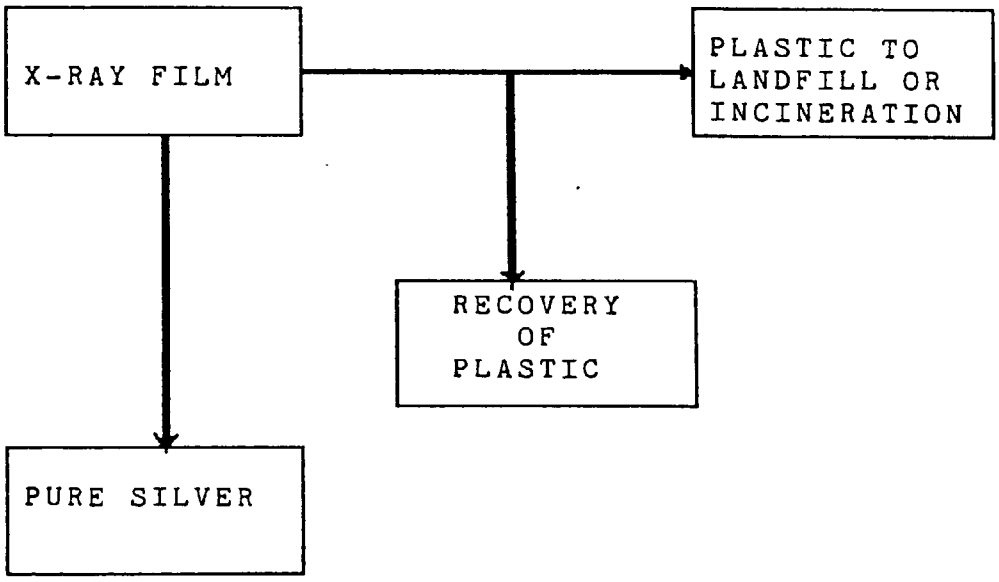
A flow-sheet and description of the proposed recycling plant, including control equipment and outline mass and energy balances, concludes the thesis.

CHAPTER ONE

INTRODUCTION

Over five million tonnes of plastic waste are produced each year in Europe, Edwards[1]. Part of this is collected with domestic refuse and is recovered as heat. Only a small fraction of it is used as a secondary raw material. New procedures are needed to regenerate plastics reclaimed from used X-ray film.

The purpose of this research work can be shown diagrammatically as follows:



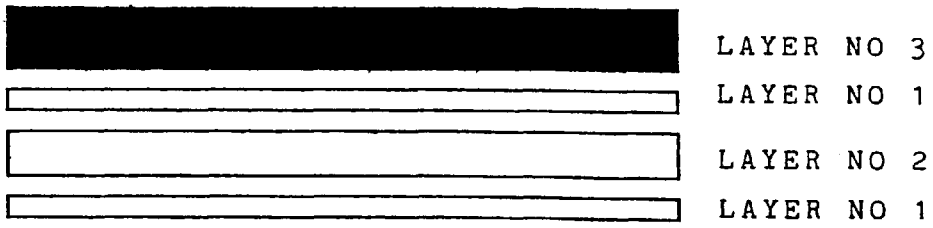
The production and consumption of X-ray film is increasing, and this will generate considerable amounts of waste and scrap that could be recycled, recovered, and transformed to useful products.

In the UK alone over five million kg per annum of used X-ray film and lithographic films from hospitals and the printing industry, is being incinerated or land filled after reclaiming the silver [1].

The type of plastic in the base plate of an X-ray and lithographic film is known as poly (ethylene terephthalate) or PET.

Exploded Diagram of X-ray Film:

Layer No. 1	Poly (vinylidene) chloride (PVDC)
Layer No. 2	Emulsion of photographic salts and blue dye
Layer No. 3	Base of Poly (ethylene terephthalate) (PET)



Any recycled material is of value only if there is a market for it, at a price that ensures profitability.

Polyethylene terephthalate polymer from X-ray and lithographic film at the present time carries no commercial value due to the following problems:

A The presence of Poly (vinylidene chloride) PVDC or commonly known as SARAN, in both top and sub layer of the base plate.

The plastics industry requires no greater than 10-30 parts per million residual poly (vinylidene chloride) to be acceptable. The presence of PVDC in the PET, above the acceptable limit, will cause malfunctioning of the extrusion equipment , used in processing.

B The presence of photographic salts.

C Blue colouration will limit its applications.

D Low intrinsic viscosity (I.V.) of the poly (ethylene terephthalate).

E Toxicity of the de-silvered film.

F The presence of paper, adhesive tapes and metal in the used film.

G The necessity of drying the end product

H The lack of an efficient and economically viable recycling process.

Failure to solve any one of the above problems will fail to produce recycled clean poly (ethylene terephthalate) from the X-ray film.

CHAPTER TWO

LITERATURE SURVEY

Various processes have been proposed for recovery of terephthalic acid either as such or in the form of its dimethylester, from poly (ethylene terephthalate). These processes include saponification with alkalis or acids. Such methods require reagents that make recovery expensive and complicated, because of the various precipitations and purifications involved.

Werke Witten[2] investigated the esterifications of PET with methanol under pressure yielding dimethyl terephthalate, but the ester obtained does not have sufficient purity for use as starting material in polycondensation. They also reported that recovery of terephthalic acid from PET, using organic solvent, is uneconomical and requires extensive plant, but Hokik, Bacak and Pitat[3] developed technology that can economically recover valuable chemicals such as terephthalic acid (TPA) and ethylene glycol (EG) from waste poly (ethylene terephthalate), (PET) by hydrolysis. The hydrolysis of PET was achieved by the action of an aqueous alkali metal hydroxide solution at a temperature of 100^{o}C and two hours to complete the reaction.

During the hydrolysis ethylene glycol was formed and the authors [3] also observed that in an aqueous alcoholic medium, having water - alcohol ratio of 1:1, higher yields of TPA can be achieved, because of more limited losses in the

filtrate and due to lower concentration of the base in the hydrolytic solution.

The reaction can proceed under atmospheric as well as under increased pressure, the latter case enabling a lowering of the alkali metal content to a minimum.

The authors [3] found that hydrolysis of PET can be carried out under a pressure up to 25000 kN/m^2.

Moreno Garcia[4] described the leaching of silver from crushed film with NaCN solution, a reaction classically used in the hydrometallugical treatment of minerals containing silver. The film pieces were treated in glass vessels with NaCN solution. The solution was shaken and hydrogen peroxide was added until the black colour of the film disappeared and the clear blue of the PET appeared with the gelatine of the film. The silver is simply recovered by electrolysis of the final solution.

The investigators Muench, Notarbartolo and Spano[5] found that the scrap left over from the production of high molecular weight synthetic polyesters, and scrap recovered from the processing of polyesters to make them into finished articles can be re-used. Whenever it is not contemplated directly to reprocess it substantially according to known methods, for instance by saponification with alkalies or acids.

The authors[5] carried out experiments, by taking 50 parts wt/wt of poly (ethylene terephthalate) scrap ground to a powder and heated under agitation at about 200°C with 78 parts wt/wt of octyl alcohol for four hours. The reaction product is filtered whilst hot and 120 parts wt/wt of clear liquid are obtained to which was added 120 parts wt/wt of methyl alcohol and 17 parts wt/wt of sodium methylate to give a pH of 9-10. The precipitated dimethylester was washed with methyl alcohol and dried, (45 parts wt/wt of ester are obtained equal to a yield of 90%). The filtrate is distilled at ambient pressure, recovering about 90% of the methanol.

The remaining solution is filtered and 1.5 parts of dimethyl ester recovered as a mixture of octyl alcohol and ethylene glycol, corresponding to 92% of the amount participating in the reaction. A residue remains from which 3 parts wt/wt of dimethyl ester are re-crystallised. The total yield was 98%.

A continuous process for recovery of dimethyl terephthalate from poly (ethylene terephthalate) waste was achieved by Marion, Measamer and Miller[6] by:-

1) Dissolving and reacting the waste with ethylene glycol.

2) Reacting the products of step (1) with an excess of methanol in the presence of an ester exchange catalyst, elevated temperature and pressure to prepare dimethyl terephthalate.

3) Deactivating the ester exchange catalyst before release of the elevated pressure.

4) Distilling excess methanol.

5) Removing solids while the solution was still hot.

6) Recovering the dimethyl terephthalate.

The authors [6] developed a continuous process where the poly (ethylene terephthalate) film and ethylene glycol are continuously fed to a two stage continuous glycolysis unit. The first stage maintained at 220 - 225^{o}C and atmospheric pressure; the waste is dissolved and partially depolymerised with ethylene glycol. The second stage, is maintained at 240^{o}C and sufficient pressure to prevent boiling of the reaction solution. The solution for the first stage is further reacted with ethylene glycol to continue depolymerisation. Sufficient ethylene glycol is fed to the unit to degrade the waste into a liquid solution. The ratio of ethylene glycol units to the terephthalate units in the solution was about 1.3 to 2.0 (wt/wt).

Due to the great amount of material involved in PET, several companies including Goodyear, Du Pont and Eastman Kodak, are actively attempting to recycle PET wastes that are currently landfilled or incinerated.

For this purpose three different types of technology have been investigated by Barna, Johnstud and Lampartor[7] direct re-use, remelting and chemical reduction. PET from bottles can be directly re-used either by blending it with a virgin stream and reforming or grinding it into small pieces for use as filler material. The other method is re-melting, which includes high pressure moulding, extrusion and depolymerisation. The authors [7] also estimated expenses to recover terephthalic acid and ethylene glycol.

In 1976, Fassell and Bridges[8] recovered silver and terephthalic acid compounds from scrap film of a light sensitive silver compound on a Mylar substrate by wet oxidation at elevated temperatures and pressure. An aqueous medium containing a silver complexing compound, such as amine or ammonia was used, and the silver recovered by electrochemical methods.

Then the solution was acidified by nitric acid to precipitate the terephthalic acid compound which was filtered off and then purified.

The residual process liquor contains biodegradable ethylene glycol (EG) which is treated by standard biological sewage treatment systems.

The authors [8] obtained the results of the TA portion of PET

24.5%, silver content of the film 1.0% and other constituents 9.0%.

A process for recovering PET scrap for re-use was achieved by Barkey and Lefferts[9]. This process involved initially degrading the PET with a lower alkyl alcohol and subsequently recovering glycol, dicarboxylic diester and alcohol from the resulting reaction mixture by distillation.

The polyester was treated with at least 70% of the amount of a phosphorus - containing compound, based on the total ester - exchange catalysts in the mixture, and minimising the repolymerisation reaction. Then the mixture was heated directly to remove alcohol, water, glycols, etc from the DMT. They also provided an improved process for recovering dimethyl and ethylene glycol from poly (ethylene terephthalate) scrap which comprises of:-

1) Forming a mixture comprising poly (ethylene terephthalate), catalyst and methanol.

2) The mixture was treated to approach equilibrium in accordance with the equation.

R COOR'	+	R" OH	=	RCOOR"	+	R' OH
(Acid)		(Glycol)		(Polymer)		(Alcohol)

3) Treating the partially hydrolysed mixture with a stoichiometric excess of a phosphorus - containing compound,

based on the total ester interchange catalyst concentration, to deactivate the ester exchange catalyst and obtain dimethyl terephthalate of sufficient purity to be directly utilisable in polyester manufacture.

PET containing polyvinylidene halides are generally used as a subbing or anchoring layer between a PET film base and a gelatin layer containing halides or other silver compounds. It has been found that the silver and silver compound containing gelatin layer, can be separated cleanly from the PET base with attendant removal of the polyvinylidene halide containing polymer from both the gelatin fractions and the polyester fraction. This is achieved by treatment of the photographic film (whether exposed or unexposed) in polar aprotic solvents. Somewhat less polar solvents, comprising cyclic compounds, hydrocarbons, esters, sulfides and ketones and mixtures of polar aprotic solvents such as sulfoxides or amides in combination with the cyclic solvents as co-solvents, can also be used.

These solvents dissolve the polyvinylidene containing polymer while not affecting materially either the polyester base or the silver compound or silver metal containing gelatin layer. Of this group of solvents, the polar aprotic solvents are the preferred species, mixtures of polar aprotic solvents and polar cyclic compounds being preferred next and cyclic organic compounds which are less polar being the least preferred, in view of the relatively high temperature

required for suitable reaction.

The preferred solvents are effective at room temperature, at elevated temperature below the boiling point of the solvent and in the vapour phase above the boiling point for the solvent. Woo, Glowe and Thornton[10], carried out experiments to remove the PVDC from scrap PET, using the above solvents. The authors [10] chopped scrap PET into approximately 5 mm pieces and fed them slowly and uniformly to a stirred solvent. The material was then allowed to digest in the solvent under slow stirring conditions for periods varying from 1 hour up to 24 hours. This solution is generally effective for dissolving the PVDC layer and separating the gelatin containing layer to produce clean PET in periods of 1 to 2 hours of digestion.

After the separation of the polyester base and the gelatin containing layers, the solution is then stirred vigorously for a period of 5 to 10 minutes with a type of spiral stirrer. Under such stirring conditions the PET is unaffected but the gelatin layers being quite brittle break up into relatively fine particles which are much smaller than the original size of the film scrap chips.

The authors [10] found that the brittleness of the gelatin layers permits the breaking up of these layers under vigorous stirring. Reaction is increased if the chopped composite photographic film is heated to a temperature of 80 to 120^{o}C

for periods of 80 minutes to 1 hour to drive out the majority of the retained water in the gelatin layer.

Similar work was carried out by Gerber and Wainer[11] by breaking down the PET for recovery of valuable constituents including the silver. The polyvinylidene chloride and the polyester were recovered by treating the chopped photographic film with solvents at elevated temperature. Both the polyester and the polyvinylidene chloride are soluble in the solvents while the gelatin and silver are insoluble under the conditions chosen. The investigators [11] carried out experiments to recover the polyester base of photographic film, by dissolving the silver bearing scrap and maintaining at the dissolving temperature for 10-20 minutes.

The silver, gelatin residue and dirt was separated by filtration and then washed with hot solvent (e.g. phenol ether). The filtrate was cooled to 10^{o}C and washed to precipitate the polyester. This temperature was maintained for 20-40 minutes to produce a PET precipitate having an eventual recovered particle size of 10 - 100 microns. The product was cooled to 25 - 35^{o}C and a higher aliphatic ketone (methylbutylketone or methylisoamylketone) was added and stirred, then the ketones were filtered and washed to yield the final PET powder. The solvents were recovered by fractional and azeotropic distillation. Recovery of silver, polyester and amino acids from processed silver halide gelatin photographic film, was investigated by Wainer[12], in

a process which involves the recycling and reconstitution of the reagents used for the removal of silver from the surface of the polyester base. This avoids pollution of water streams and the atmosphere, and contributes to the overall economics of the process, and to recovery of a number of valuable by products, other than polyester which would normally be voided to the sewer. Polyester was also recovered by Thornton and Glowe[13] where the contaminates were removed from the polyester film base by combining the polyester photographic film scrap with an aqueous solution of mono-ethanolamine containing 2 to 15% by weight of water, and having a temperature between 100 and 170^{o}C for sufficient time to remove both silver and coatings. Other methods which have been proposed by Phillips[14] for recovering photographic support material, involve using enzymes, where the photographic film was agitated in a wash tank containing warm water at about neutral pH and containing at least one enzyme from the following group:- protease, amylase and adipase. The enzymes attack the adhesive and organic layers on the plastic base, in order to loosen and remove these materials. The film is then placed in a rinse tank containing a weak aqueous glycol solution which is agitated. Finally the film is removed from the rinse tank and dried. Liquid was removed from the wash tank and treated to recover silver. Du Pont[15] suggested, that in order to recover the polyester film base from photographic film coated with a tricomponent, the authors [15] recommended treatment with alkali metal hydroxide or alkaline earth metal hydroxide

solutions with 50% weight/volume aqueous solution, at temperatures up to 130°C for a period of at least 1 minute. The authors [15] obtained the following results:-

Yield strength	75 - 85 MN/m^2
Break strength	90 - 98 MN/m^2
Modulus	2700 - 3300 MN/m^2

CHAPTER THREE

PROPERTIES OF PVDC AND PET

3.1 Poly (vinylidene chloride) PVDC

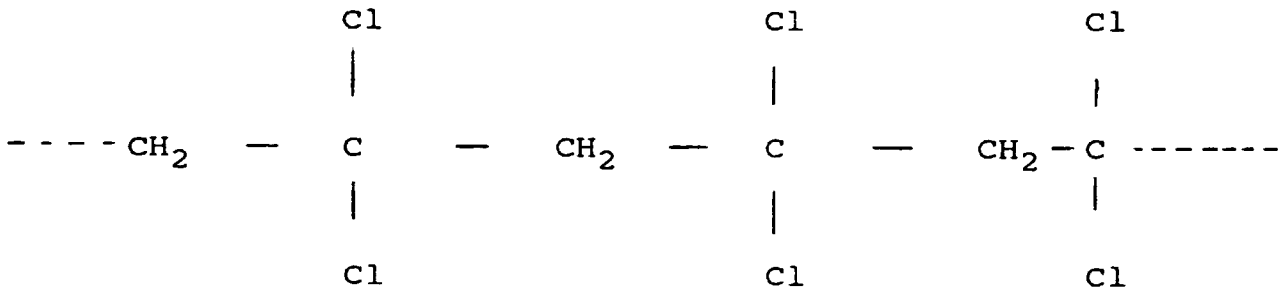
3.2 Poly (ethylene terephthalate) PET

3.1 Poly (vinylidene chloride)

3.1.1 Structure

The chemical composition of PVDC has been confirmed by various techniques, including elemental analysis and X-ray diffraction analysis.

The polymer chain is made up of monomeric vinylidene chloride units (1,1 - dichloroethylene) which are joined head-to-tail with a configuration of carbon atoms [16].



Variations in structure can come about by head-to-tail addition, branching or degradation reaction.

This includes such reactions as thermal dehydrochlorination. The infrared spectra of poly (vinylidene chloride) often shows traces of both unsaturation and carbonyl absorption. The slightly yellow tinge comes from the same source; the pure polymer is colourless. Elemental analysis for chlorine is normally slightly lower than the theoretical value which is 73.14%.

3.1.2 Physical Properties

The physical properties of the commercial poly (vinylidene chloride) are summarised in the tables below [16, 17, 18].

Table (1)

Molecular weight	10,000 to 100,000
Decomposition temperature, ^{o}C	225
Melting point, ^{o}C	202
Appearance	Clear
Density, g/cm^3, at $20^{o}C$	1.21
Refractive index (crystalline) N_D	1.63
Water absorption, 27 hours immersion %	0.1 or less
Softening Point, ^{o}C	115 - 140

3.1.3 Solubility

PVDC is not soluble in common solvents at room temperatures. Five classes or specific solvents were observed that could dissolve PVDC at low temperatures, these include:- sulphoxides, dialkyl amides, alkyl lactams and cyclic ketones. PVDC acts as a weak Lewis acid in these solutions [16, 19]. It will swell or soften only in oxygen - bearing organic solvents (such as cyclohexanone and dioxane). In cases where the solvent is a base such as pyridine, the polymer decomposes even at low temperatures. These compounds are not categorised as solvents even though they dissolve the polymer.

3.1.4 Barrier Properties

PVDC polymer is more impermeable to a wider variety of gases and liquids than other polymers.

This is a consequence of the combination of high density and high crystallinity in the polymer [16, 19].

Table (2)

The Permeability of Saran to Various Gases

Gas	Temperature ^{o}C	$PX10^{-13}$ $(cm^3.cm)/(cm^2\text{-}sec.kPa)$
N_2	25	0.75
O_2	25	1.5
CO_2	25	9.0

3.1.5 Mechanical Properties

The estimated mechanical properties of poly (vinylidene chloride) are [16, 18].

Table (3)

Tensile strength, MPa	
unoriented	34.5 - 69.0
oriented	207 - 414
Elongation, %	
unoriented	10 - 20
oriented	15 - 40
Softening range (heat distortion) ^{o}C	100 - 150
Flow temperature, ^{o}C	185
Brittle temperature, ^{o}C	-10 to +10

3.1.6 Degradation Chemistry

Poly (vinylidene chloride) is thermally unstable and when heated above 125 ^{o}C, evolves HCl. Degradation can be effected by heat, ultraviolet radiation, ionising radiation (X-ray) and basic reagents, [20].

The reaction is normally described as a two-step process:

Formation of a conjugated polyene.

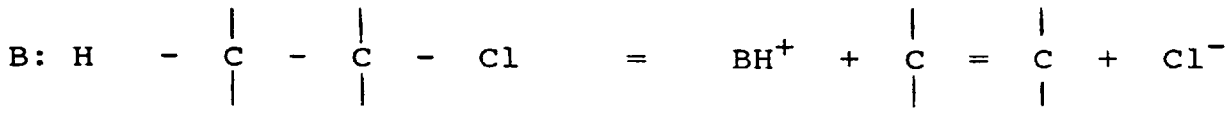
$$---(CH_2 - CCl_2)_n--- \xrightarrow{\text{Fast}} ---(CH = CCl)_n + n\ HCl$$

Carbonisation

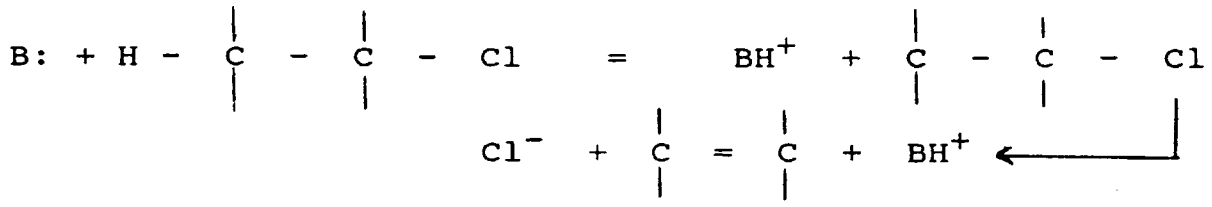
$$---(CH_2 - CCl)_n--- \xrightarrow{\text{Slow}} 2nC + nHCl$$

The above degradation reaction is heterogeneous with the polymer present as a solid phase.

Hot concentrated bases will decompose the polymer over a long period of time. Weak bases such as ammonia, amines, polar aprotic solvents, also accelerate the decomposition of PVDC by concerted elimination.



Carbonation intermediate



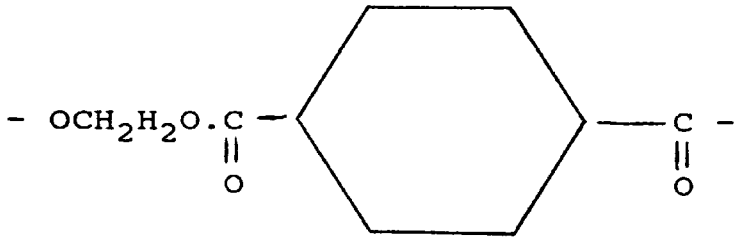
In the presence of oxygen degradation gives rise to the C = O group, [21] whose concentration can be followed by infra-red spectroscopy. The colouration is probably due to a mixture of oxidation and unsaturation, with mild degradation there is usually an increase in the dilute solution viscosity of the polymer.

3.2 Poly (ethylene terephthalate)

3.2.1 Structure

Poly (ethylene terephthalate) can be considered as a polycondensation product from Ethylene Glycol (EG) and Terephthalic Acid (TA).

It has a regular linear structure with the connecting ester carbon attached directly to the aromatic ring in the backbone of the molecular chain. PET has the following repeat unit (22, 23).



$C_{10}H_8O_4$, Molecular weight = 192

Molecular weight of commercial polymers: Number - average 15 - 20,000 (degree of polymerisation 80 - 105) weight average, 20 - 30,000 (degree of polymerisation 105 - 155).

Table (4)

3.2.2 **Physical Properties of PET Film**

The following is of virgin PET film [22, 24].

Melting Point, ^oC	250 - 265
Specific heat, cal/g/^oC	0.315
Shrinkage % (30 min @ 150 ^oC)	2 - 3
Density, g/cm^3 at 25 ^oC	
Amorphous	1.335
Crystalline	1.455
Moisture Absorption, (immersion for 24 hours at 23 ^oC)	- 0.8%
Gas Permeability, (cm^3.cm)/(cm^2 - 24hr.kPa) at 23^oC	
Carbon Dioxide	16
Hydrogen	100
Nitrogen	1
Oxygen	6

3.2.3 **Chemical Properties**

Dissolved by [22, 23]

1. Phenols (m - cresol, 0 - chlorophenol) and phenol/ chlorinated hydrocarbon mixtures (1/3 vol/vol).
2. Phenol/tetrachloroethane.
3. Acetonylacetone.
4. Dichloroacetic acid.
5. Concentrated sulphuric acid (with decomposition).
6. Hot benzyl alcohol.
7. Benzyl acetate.

Relatively unaffected by [22, 23]

1. Hydrocarbons, esters and dry cleaning solvents.
2. Formic acetic, phosphoric and hydrofluoric acids.
3. Resistance to bleaching solutions.
4. Reducing agents and mild alkalis (e.g. Na_2 CO_3).
5. Moderate exposure to mineral acids.

Decomposed by

1. Hot alcoholic alkalis.
2. Hot aqueous alkalis (e.g. dil NaOH, particularly in the presence of quaternary ammonium compounds).
3. Hot amines.
4. Mineral acids cause loss of strength, dependent on concentration and on time and temperature of exposure e.g. tensile strength falls to 50% after 50 hours at 100^{o}C in 7.5% HCl, 16% HNO_3 or 45% in H_2SO_4.

5. PET decomposed by boiling in a glycol or by heating under pressure with methanol (e.g. at 180°C) or water (at 200°C).

Amorphous PET is much less resistant to chemical attack than the usual oriented crystalline films.

Table (5)

Chemical Resistance of PET Film

Chemical Resistance

	Tensile strength retained %	Elongation retained %	Tear strength retained %	Days immersed at 20°C
Acetic Acid (glacial)	100	100	100	31
Hydrochloric Acid (10%)	100	100	100	31
Sodium Hydroxide (2%)	100	100	70	31
Ammonium Hydroxide (conc.)	0	0	0	3
Trichloroethylene	100	100	100	31
Hydrocarbon	92	88	87	500 hr at 100°C baked 168 hour at 150°C

3.2.4 Mechanical Properties

The crystalline form of PET is very brittle and opaque and the amorphous form is clear but not very tough.

Generally, the tendering process is preferred for biaxially orienting polyethylene terephthalate [22, 23] for base films due to the following [23, 24, 25]:-

1. Highly resistant to most organic and mineral acids.
2. No plasticisers and very low moisture retention (less than 0.5% at room temperature and 50% relative humidity).
3. High strength, toughness and durability, excellent flex life.
4. Large number of specific modifications available.
5. Excellent electrical properties.

Table (6)

Typical Properties of PET Film

Elastic Modulus (Young's) (MN/m^2)	4400
Tensile Strength (MN/m^2)	124
% Elongation	70
I.V. ml/g	0.9

CHAPTER FOUR

Experimental Work

4.1 Removal of Silver and Silver analysis

4.2 X-ray Base Plate

4.3 Determination of Papers and Adhesive Tapes

4.4 Water Absorption

4.5 Removal of PVDC Coating

4.6 Determination of PVDC

4.7 Determination of I.V.

4.8 Tensile Strength and Elongation

4.1 Removal of Silver and Determination of Silver Content

Procedure

The shredded sample of film was leached with an alkaline oxidising solution of sodium cyanide.

Approximately 60 to 80g of sample material was weighed within ± 0.01g and transferred to a 1 litre beaker (tall size) which was pre-weighed.

Leaching solution (800 ml) was then added. The composition of the leaching solution was [26]:-

NaOH	50 g
NaCN	100 g
Meta nitrobenzenesulfonic acid	20 g
Deionised water	5 litres

The solution was stirred with a glass rod in order to wet the small pieces of film. The sample was leached for two hours with stirring.

The solution was filtered through No. 1 Whatman filter paper of 9 cm diameter into a 1 litre volumetric flask.

Using a PU9100 Atomic Absorption Spectrophotometer with the following working conditions:-

Single element 1 amp current	3 ma
Fuel	Acetylene
Flame stoichiometry	Oxidising

Wavelength	338.3 nm
Spectral band pass	0.2 nm
Range	3 - 12 ppm
Support	Air

Safety Considerations

Decomposition of the cyanide solutions after the test [27] was carried out.

Results

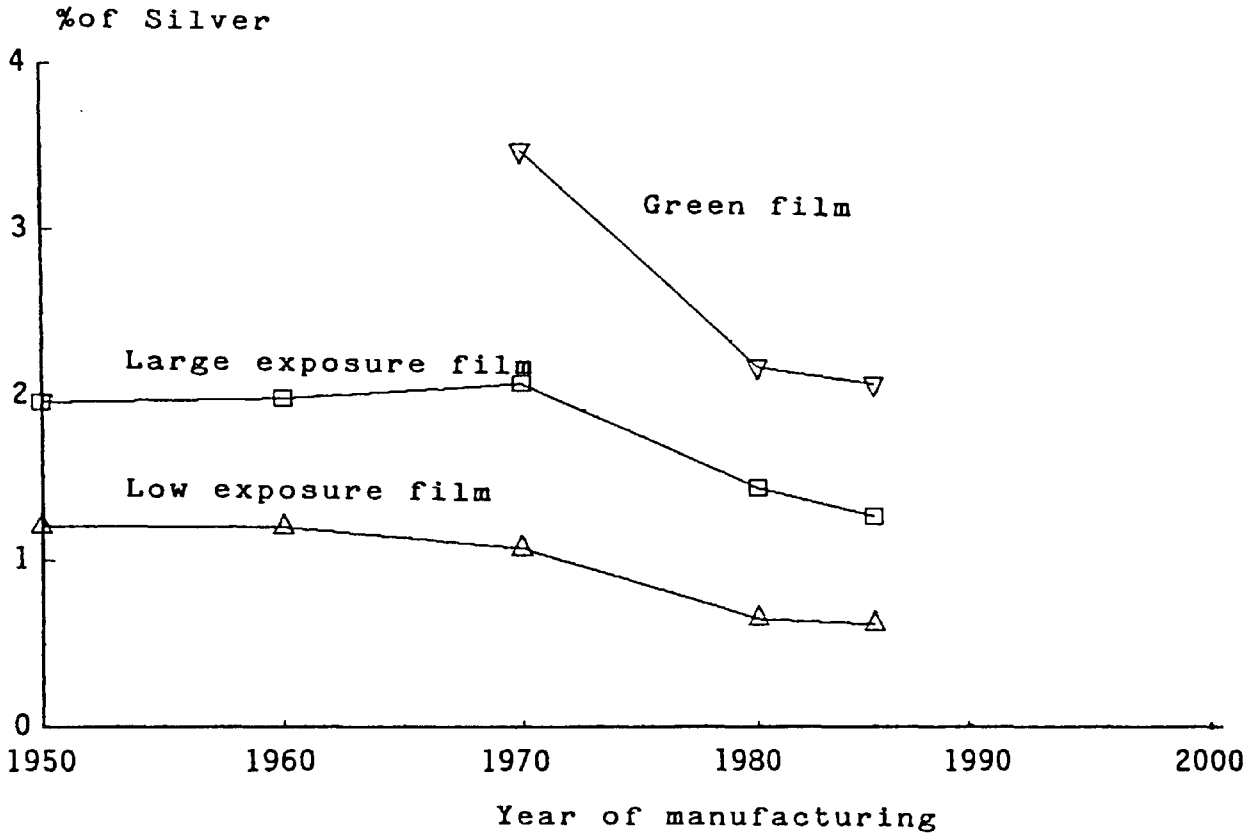
Table (7)

Type of film	Year	Weight (g)	Silver Content (g)	Percentage of Silver
Large Exposure	1950	80.00	0.9600	1.20
Low Exposure	1950	80.00	0.5680	1.96
Large Exposure	1960	50.00	0.6000	1.20
Low Exposure	1960	50.00	0.9950	1.99
Large Exposure	1970	60.00	0.6480	1.08
Low Exposure	1970	100.00	2.0900	2.09
Large Exposure	1980	70.00	0.4620	0.66
Low Exposure	1980	30.00	0.4350	1.45
Green Film	1980	50.00	1.1000	2.20
Large Exposure	1985	80.00	0.5040	0.63
Low Exposure	1985	60.00	0.7680	1.28
Green Film	1985	50.00	1.0500	2.10

See samples in Appendix A page 108

Figure No. (1)

Graph showing the % of Silver vs Year of Manufacturing



4.2 X-ray Film Base Plate

Poly (ethylene terephthalate) PET and cellulose Triacetate CTA are two types of plastics used in the manufacturing of X-ray base plates, which they are investigated by the following methods.

4.2.1 Density

A number of X-ray plates were taken from different periods, and after de-silvering them using sodium hypochlorite, and the surface of the film was delaminated with an organic solvent namely tetrahydrofuran. The plates were dried and weighed and then the density was determined.

Results

Table (8)

Number of X-ray plates taken	Weight of Plates (g)	Average weight per Plates (g)	Density kg/m^3	Period
53	1706	32.2	2810	1950-1959
66	2165	32.8	2860	1960-1969
93	2827	30.4	2650	1970-1979
100	2960	29.6	2490	1980-1985

4.2.2 Infra-red Reflectance (ATR)

The infra-red analysis was of a quantitative nature and involved standard techniques such as the preparation of film discs in order to obtain spectra of the samples under analysis. Once obtained, these spectra were compared with

reference spectra prepared in a similar manner to the samples.

The results are shown in Figure 2 and Figure 3.

Figure No(2)
Infra-red spectra for PET

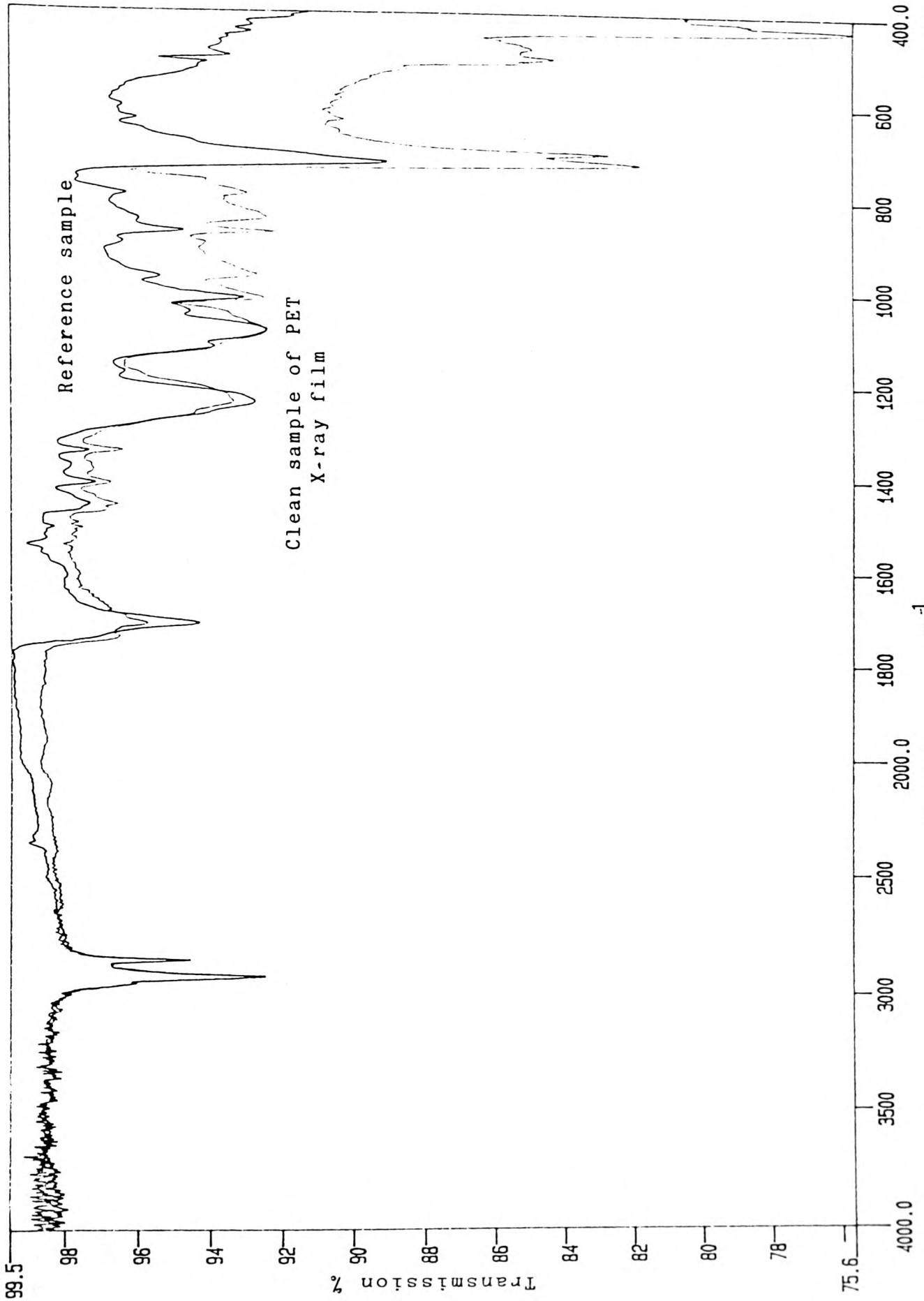
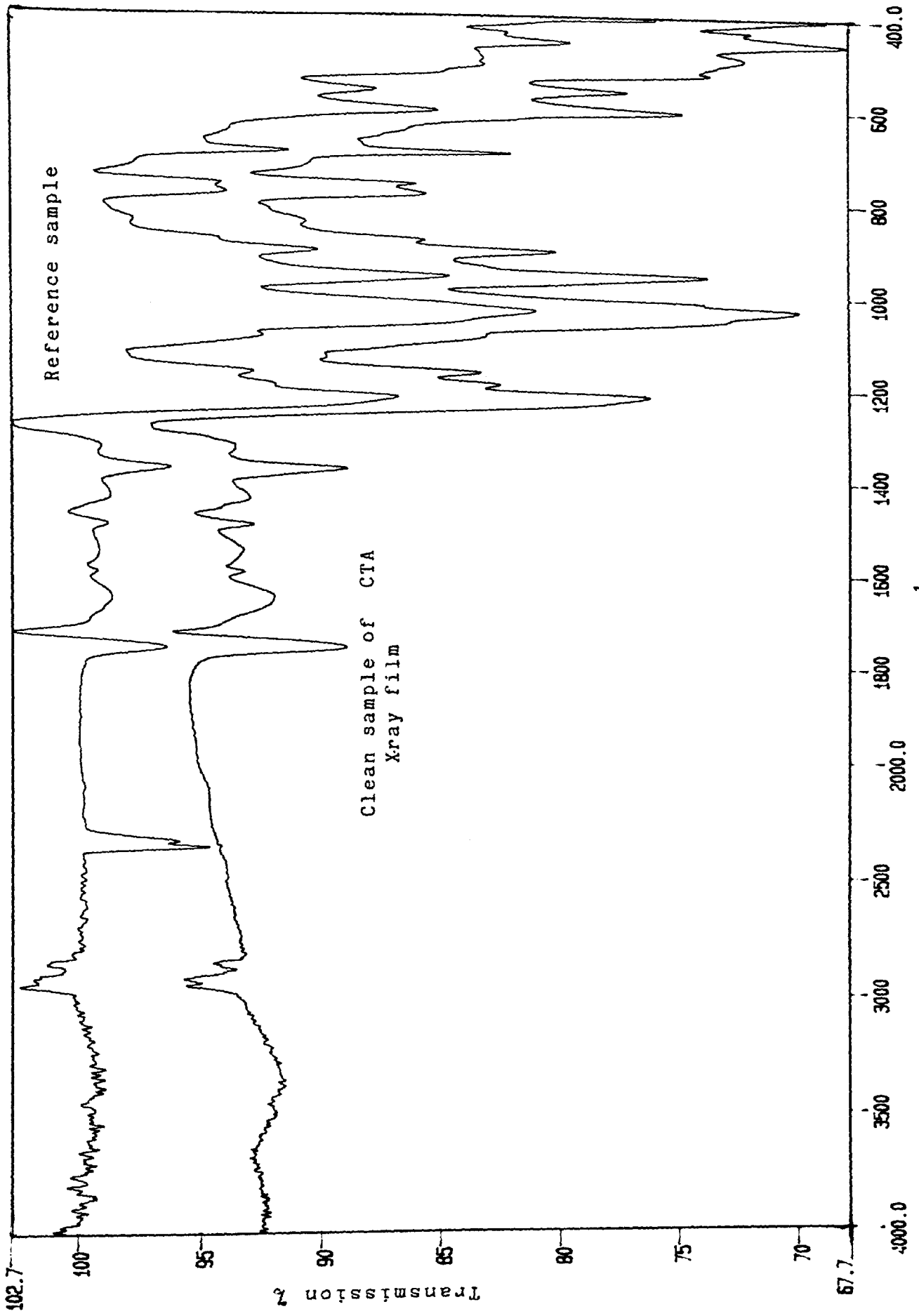


Figure NO(3)

Infra-red spectra for CTA



4.3 Determination of Papers and Adhesive Tapes

A sample of X-ray film was taken and weighed before separating the papers and tapes. The separation was carried out physically by hand and each component was weighed separately.

Results

Table (9)

Run	Weight of Sample (kg)	Weight of X-ray film (kg)	Weight of Tape (kg)	Weight of Paper (kg)
1	30	27.50	0.45	2.05
2	50	45.60	0.75	3.65
3	63	57.60	1.00	4.40
4	65	57.50	0.97	4.53
5	85	78.00	1.14	5.86

Calculations

Table (10)

Run	% X-ray film	% Adhesive tape	% Paper
1	91.7	1.5	6.8
2	91.2	1.5	7.3
3	91.4	1.6	7.0
4	91.5	1.5	7.0
5	91.7	1.3	6.9

4.4 Water Absorption

This experiment covers the determination of the relative rate of absorption of water by the X-ray base plates and their pellets when immersed in water or exposed to the atmosphere at normal conditions.

This test has two significant functions:-

A As a guide to the proportion of water absorbed by Poly (ethylene terephthalate) and consequently, the relationship between moisture content and its mechanical properties.

B As a control test on the uniformity of the product.

Theory

The rate of water absorption may be widely different through each edge and surface. It may be slightly greater through cut edges than through pelletised surfaces. Consequently, attempts to correlate water absorption with the surface area must generally be limited to closely related materials.

For materials of widely varying density, the relation between water absorption values and a volume as well as a weight basis may need to be considered.

Calculation

Percentage increase in weight

$$= \frac{\text{Wet Weight - Conditioning Weight) x 100}}{\text{Conditioning Weight}}$$

Percentage of soluble matter lost

$$= \frac{\text{Conditioning Weight - Reconditioning Weight) x 100}}{\text{Conditioning Weight}}$$

Reconditioning Weight: This is the dry weight of the specimen after immersion, for the same temperature and time as used in the original drying period of the conditioning. The percentage of water absorbed = percentage of increase and percentage of matter lost. If the weight of reconditioning exceeds the conditioned weight, then the percentage of soluble matter lost is considered to be nil [27].

Preparation of the Sample

The test sample is placed in a dry air swept oven (less than 3% relative humidity) at ± 39.5°C for 24 hours. Then the sample was removed from the oven and cooled in a desiccator to room temperature and immediately weighed to the nearest 0.001 g [27].

Three specimens were taken:

Specimen No. S1

Represents film before the process, i.e. still containing the silver emulsion coating.

Specimen No. S2

Represents film after removing the silver layer and immersed in cyclohexanone at room temperature for 15 minutes or longer

to dissolve the coating entirely from the PET, and then it was rinsed in ethyl acetate and water.

Specimen No. S3

Represents clean pelletised X-ray film after it has been de-silvered and delaminated.

All specimens should be oil and wax free.

Procedure

4.4.1 **Immersion in Water**

The dry samples were fully immersed in a container of deionised water at a temperature maintained at 23 ± 1^{o}C for 2 hour and 24 hour respectively. The samples were then removed from the warm water, one at a time, and cooled in distilled water maintained at 20^{o}C. After 15 minutes the samples were removed from the cold water and the surface was wiped free of the water with a dry cloth and weighed to the nearest 0.0001 g.

4.4.2 **Moisture Permeability**

The dried sample was placed over the top of an aluminium cap and left in the storage area (normal conditions, with temperature about 15 ^{o}C) for 1 day, 7 days, 30 days, 90 days and 180 days exposed to the air. The samples were then weighed to the nearest 0.0001 g.

In the specimens (S1, S2, S3), the samples were then placed

in a dry (less than 3% relative humidity) air swept oven at 39.5°C for 24 hours, then the sample was cooled, in a desiccator to room temperature and weighed to the nearest 0.0001 g.

The above procedure was repeated three times and an average result was taken for each sample.

Results

Water Immersion

Table (11)

2 Hours Immersion

Specimen Number	Wet Weight (g)	Conditioning Weight (g)	Reconditioning Weight (g)	% of Increase in Weight	% of Soluble Matter Lost	% of Water Absorbed
S1	20.3241	20.3239	20.3420	0.00	0.00	0.00
S2	20.0840	20.0820	20.1111	0.01	0.00	0.01
S3	20.1400	20.1398	20.1461	0.00	0.00	0.00

Table (12)

24 Hours Immersion

Specimen Number	Wet Weight (g)	Conditioning Weight (g)	Reconditioning Weight (g)	% of Increase in Weight	% of Soluble Matter Lost	% of Water Absorbed
S1	20.1000	20.0199	20.0336	0.4001	0.00	0.4001
S2	19.8191	19.7278	19.7238	0.4528	0.203	0.4831
S3	19.9841	19.9797	20.0011	0.0221	0.00	0.0221

Table (13)

Moisture Permeability

Specimen Number	Period of Exposure (Days)	Moisture Weight (g)	Conditioning Weight (g)	Reconditioning Weight (g)	% of Increase in Weight	% of Matter Lost	% of Water Absorbed
S1	1	180.3014	180.3012	180.3023	0.0001	0.0000	0.0001
S2	1	190.1391	190.1391	190.3641	0.0000	0.0000	0.0000
S3	1	195.0013	195.0012	195.0199	0.0000	0.0000	0.0000
S1	7	179.0301	179.0068	179.0069	0.0130	0.0000	0.0130
S2	7	165.1952	164.6986	164.6980	0.3015	0.0004	0.3019
S3	7	182.6636	182.6634	182.6634	0.0001	0.0000	0.0001
S1	30	178.1122	177.9376	177.9400	0.0981	0.0000	0.0981
S2	30	166.3320	165.4222	165.4232	0.5500	0.0000	0.5500
S3	30	159.5631	159.5117	159.5090	0.0322	0.0018	0.0340

Table (14)

Moisture Permeability

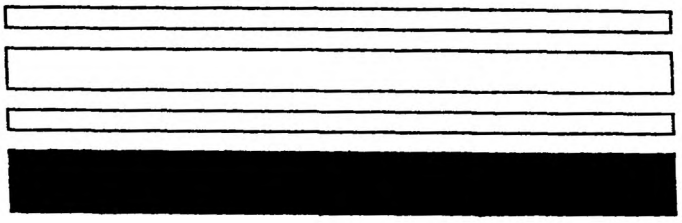
Specimen Number	Period of Exposure (Days)	Moisture Weight (g)	Conditioning Weight (g)	Reconditioning Weight (g)	% of Increase in Weight	% of Matter Lost	% of Water Absorbed
S1	90	175.6831	175.4541	175.4434	0.1305	0.0061	0.1366
S2	90	186.0092	184.8447	184.8498	0.6300	0.0000	0.6300
S3	90	173.5819	173.5050	173.5056	0.0443	0.0000	0.0443
S1	180	188.6511	188.3872	188.3882	0.1401	0.000	0.1401
S2	180	177.9932	176.7840	176.7881	0.6840	0.0002	0.6842
S3	180	169.7539	169.6718	169.6718	0.0484	0.000	0.0484

4.5 **Removal of Poly (vinylidene chloride) Coating**

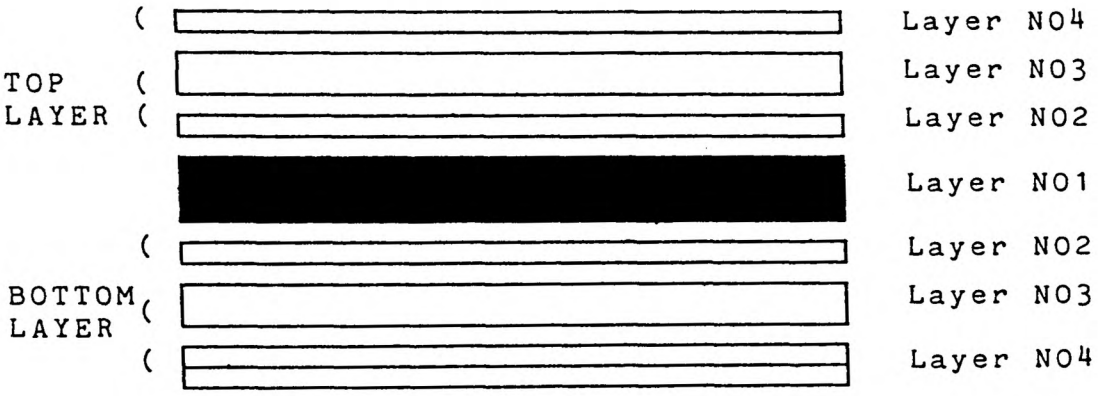
During the manufacturing of X-ray film, PVDC (Saran) is applied before the base film is wound into rolls [27, 29], this process produced a great deal of unrecyclable PET waste. So the coating must be removed without damaging the PET.

Economic and chemical considerations require that there be little or no decomposition of the solvent media, or significant reaction of the solvent media with the X-ray film raw material. This is because it is an economic necessity that the solvent be capable of being recovered in fully useful form for recycling.

SINGLE EMULSION FILM



DOUBLE EMULSION FILM



Layer 1: Poly (ethylene terephthalate) PET

Layer 2: Poly (vinylidene chloride) PVDC Sub-Layer

Layer 3: Gelatin - Silver Halide, light sensitive emulsion layer

Layer 4: Poly (vinylidene chloride) PVDC top layer

The sub-layer of PVDC (Saran) is applied to improve the adhesion of the light sensitive emulsion to the film base PET and it is chemically inert towards it.

The top layer of PVDC is added for moisture and gas protection due to its low permeability to a wide range of gases and vapours and it is also hydrophobic.

There are two ways of decoating Saran from PET X-ray film base.

1. Solution Method
2. Delamination/Segregation Method

4.5.1 Solution

Poly (vinylidene chloride) can be dissolved away from the PET substrate using a number of solvents [19].

Cyclohexanone and chlorobenzene were tried to remove the PVDC from X-ray plates.

Procedure

Samples of 1 kg of de-silvered X-ray film were shredded in two ways:-

(i) knife shredding

(ii) hammer shredding

The size of the particles was 5 cm. The samples were then

placed in the above solvents and the contents were stirred continuously for 15 minutes, to ensure complete contact of solvents with the pieces of X-ray film.

Results

Table 15 shows the effect of different cutting methods on the decoating.

Table (15)

Specimen	Solvent Used	Knife Cut	Hammer Cut
1	Cyclohexanone	Unsatisfactory	----------
2	Cyclohexanone		Satisfactory
3	Chlorobenzene	Unsatisfactory	----------
4	Chlorobenzene		Satisfactory

4.5.2 **Delamination/Segregation**

In this method the PVDC was removed in two steps, a delamination/segregation process which was carried out in a single unit operation.

The segregation step of PET from PVDC and other contaminants such as paper, metals involves a flotation process, where the PET sinks and the Saran and other contaminants float to the top of the bath.

Procedure

De-silvered X-ray film was shredded into small pieces using a hammer mill. The film was treated with a hot solution of sodium hydroxide and wetting agent for 2 hours with continuous stirring.

The material was then treated with another solution of 40% water - sodium bromide [28] at a temperature less than 15°C with air bubbles introduced from the bottom through spargers. This process was continued for 2 hours to produce PVDC and adhesive paper floating on the top, while PET and metals sank to the bottom.

Safety Considerations

1. The sodium hydroxide was used in small quantities (0.5 - 1.0 g/l) so that little effluent pollution problems were anticipated.

2. The wetting agent used was a polyglycol ether of a fatty alcohol (known as MIRAVON B79R - RTZ chemicals) with flash point of 100°C, low toxicity of LD_{50} above 2000 mg/kg and non-corrosive.

Results

Table (16)

Run	% of Wetting Agent	NaOH g/l	Temperature ^{o}C	Remarks
1	0.1	0.5	50	No swelling on the surface
2	0.1	1.0	50	Partial swelling
3	0.1	0.5	60	Partial swelling
4	0.2	1.0	60	Complete swelling
5	0.2	0.5	70	Complete swelling
6	0.2	1.0	70	Complete swelling
7	0.1	0.5	70	Complete swelling

4.6 Determination of Poly (vinylidene chloride)

PVDC or Saran can be determined in a sample of X-ray film by:

A Staining with triethylene tetramine which colours the residual PVDC brown.

B Melting the chip in an aluminium dish at 300^{o}C for 15 minutes.

C Carrying out chlorine analysis.

Method 'A' was used on the flakes to give a quick indication of the contamination of the PET with PVDC.

Method 'B' was used before the extrusion process of PET.

Method 'C' was used to determine the PVDC in the PET sample.

Theory

The sodium metal reacts with the chlorine atoms in the PVDC to form sodium chloride.

The percentage of chlorine in the dry silver chloride was 24.74% and PVDC contains 73.14% chlorine [24].

Procedure

A sample of dry X-ray PET film was weighed and placed in a test tube with a small piece of sodium metal using a pair of tweezers and dry knife to cut the sodium. The tube was heated carefully in a gas flame with the open end of the tube pointed away, from the face, the heat was continued until the metal melted, then the tube was quenched rapidly by submerging the hot end in a strong beaker containing approximately 10 ml of distilled water (ordinary water is so polluted, that it will make errors in the test results). Obviously, the tube was shattered in the water and the products of the heating dissolved in the water.

The liquid was stirred carefully with a long glass rod to make sure that all of the metal was reacted. Then the liquid was filtered through unbleached paper to remove the solids.

Using HACH DR/2000 Spectrophotometer with the following working conditions:

Wavelength	530 nm
Time	3 minutes
Solvents (mixture)	Perchloric acid and Mercuric thiocyanate

Results

A **Unexposed X-ray film (green film)**

Table (17)

Run	Weight of Sample (g)	% of Cl_2	% of PVDC	Weight PVDC (PPM)
1	1.0971	2.01	2.75	30216
2	1.3673	2.09	2.85	38966
3	1.8007	2.03	2.78	50041
4	1.060	2.02	2.76	27755
5	1.0792	1.98	2.48	26798

B **De-silvered X-ray Film**

Table (18)

Run	Weight of Sample (g)	% of Cl_2	% of PVDC	Weight PVDC (PPM)
1	1.5320	1.10	1.51	23106
2	1.3221	0.77	1.05	13946
3	1.3330	1.00	1.37	18184
4	1.0786	0.97	1.33	14355
5	1.6707	1.03	1.41	23517

C **De-silvered and Delaminated X-ray Film**

Table (19)

Run	Weight of Sample (g)	% of Cl_2	% of PVDC	Weight PVDC (PPM)
1	2.0030	0	0	0
2	4.9836	0	0	0
3	4.9830	0	0	0

4.7 Determination of Intrinsic Viscosity (I.V)

The IUPAC term for the I.V. is the Limiting Viscosity Number. It is the simplest diagnostic tool for estimating the molecular weight of a plastic.

The method consists of simply measuring the flow time through a capillary viscometer of a dilute solution of a polymer and of the pure solvent at specified conditions of temperature and concentration.

There are four flow types [30]

1. Newtonian: Oils, water, aqueous solutions of low - molecular weight substances.

2. Pseudo-plastic: Solutions of high polymer chain molecules.

3. Plastic: Suspensions and emulsions with solvate envelopes, the solvated particles of the disperse phase touching each other.

4. Dilatant: (Turbulent) dispersions without solvate envelopes the particles almost touching each other, i.e. a tightly packed system.

Theory

The relative viscosity is defined as the quotient of the viscosity of the solution N_s and the viscosity of the solvent N_{so}

$$N_r = N_s/N_{so}$$

Another measure of the increase in viscosity by a high molecular weight solute is the specific viscosity.

$$N_{sp} = N_r - 1$$

Then the limiting viscosity is one when either N_{sp}/C or $(\mathrm{Ln}N_r)/C$ is extrapolated to zero concentration.

$$\text{I.V.} = [N] = \lim_{C \to 0} \frac{N_{sp}}{C} = \lim_{C \to 0} \frac{\mathrm{Ln}\, N_r}{C}$$

C is the polymer concentration g/ml.

Since the relative viscosity is dimensionless, the units for [N] are those of reciprocal concentration. The (IUPAC) concentration unit is g/ml.

I.V. Units are ml/g

Procedure

The method [32] covers the determination of the dilute solution - viscosity of polymers.

A sample X-ray film (PET) was weighed and dissolved in a solution of o - chlorophenol and transferred into a nitrogen purged 100 ml volumetric flask (the flask was purged to prevent the oxidation of the sample).

The sample was stirred continuously until the PET dissolved completely.

The volumetric flasks containing the solutions and the pure o - chlorophenol solvent were placed in a constant temperature water bath at 30 ^{o}C. o - chlorophenol was added to each flask to make up the total volume in each flask to 100 ml and the solution was mixed well.

When the temperature equilibrium has been reached after approximately 30 minutes, the liquid level in the viscometer was brought above the upper graduation mark by means of slight nitrogen pressure applied to the arm opposite the

capillary.

The timer was started exactly as the meniscus passes the upper graduation mark and was stopped as it passed the lower mark.

This procedure was repeated for each sample and for the pure solvent.

The results were plotted in a computer using Technicurve program.

Safety Considerations

o - chlorophenol ClC_6H_4OH (boiling point 175 ^oC), is toxic and appropriate measures were taken to avoid breathing its vapours, or contact of the liquid with skin or on eyes.

Moist X-ray Film (flake form)

The flake sample was left in storage conditions of ± 20°C for 60 days before the test was carried out.

Table (20)

Run	C (g/100ml)	N_r	$\frac{N_r - 1}{C}$
1	0.23	1.1473	0.64
2	0.33	1.2146	0.65
3	0.41	1.2584	0.63
4	0.49	1.3380	0.69
5	0.60	1.4200	0.70
6	0.74	1.5327	0.72

Linear Regression Results (Figure 4)

Slope	0.177
$\frac{N_r - 1}{C}$	0.589
Correlation coefficient	0.894
Standard error	0.018

Dry X-ray Film (flake form)

The flake sample was dried in an oven at a temperature of ± 50°C for 24 hours prior to the test.

Table (21)

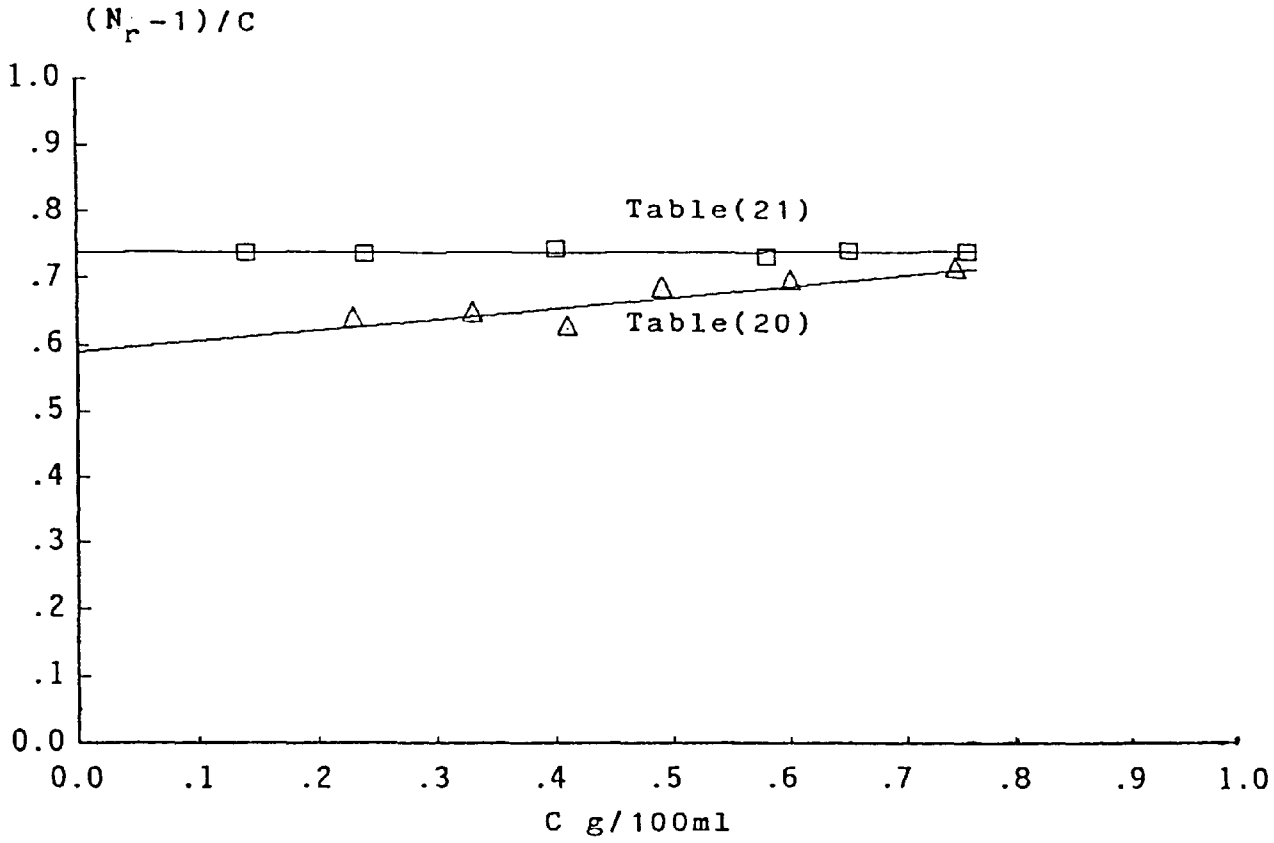
Run	C (g/100ml)	N_r	$\frac{N_r - 1}{C}$
1	0.14	1.1037	0.74
2	0.24	1.788	0.74
3	0.40	1.3020	0.75
4	0.58	1.4292	0.74
5	0.65	1.4876	0.75
6	0.75	1.5624	0.75

Linear Regression Results (Figure 4)

Slope	0.015
$\frac{N_r - 1}{C}$	0.738
Correlation coefficient	0.636
Standard error	0.005

Figure Number (4)

Graph to determine the I.V. of PET flake



Moist X-ray Film (pellet form)

The pellet sample was left in ordinary storage conditions of ± 20°C for 60 days prior to the test.

Table (22)

Run	C (g/100ml)	N_r	$\frac{N_r - 1}{C}$
1	0.15	1.0656	0.44
2	0.32	1.1473	0.46
3	0.39	1.0209	0.51
4	0.63	1.3591	0.57
5	0.72	0.4247	0.59

Linear Regression Results (Figure 5)

Slope	0.279
$\frac{N_r - 1}{C}$	0.391
Correlation coefficient	0.983
Standard error	0.014

Dry X-ray Film (pellet form)

The pellet sample was dried in an oven at a temperature of 150°C for 24 hours, prior to the test.

Table (23)

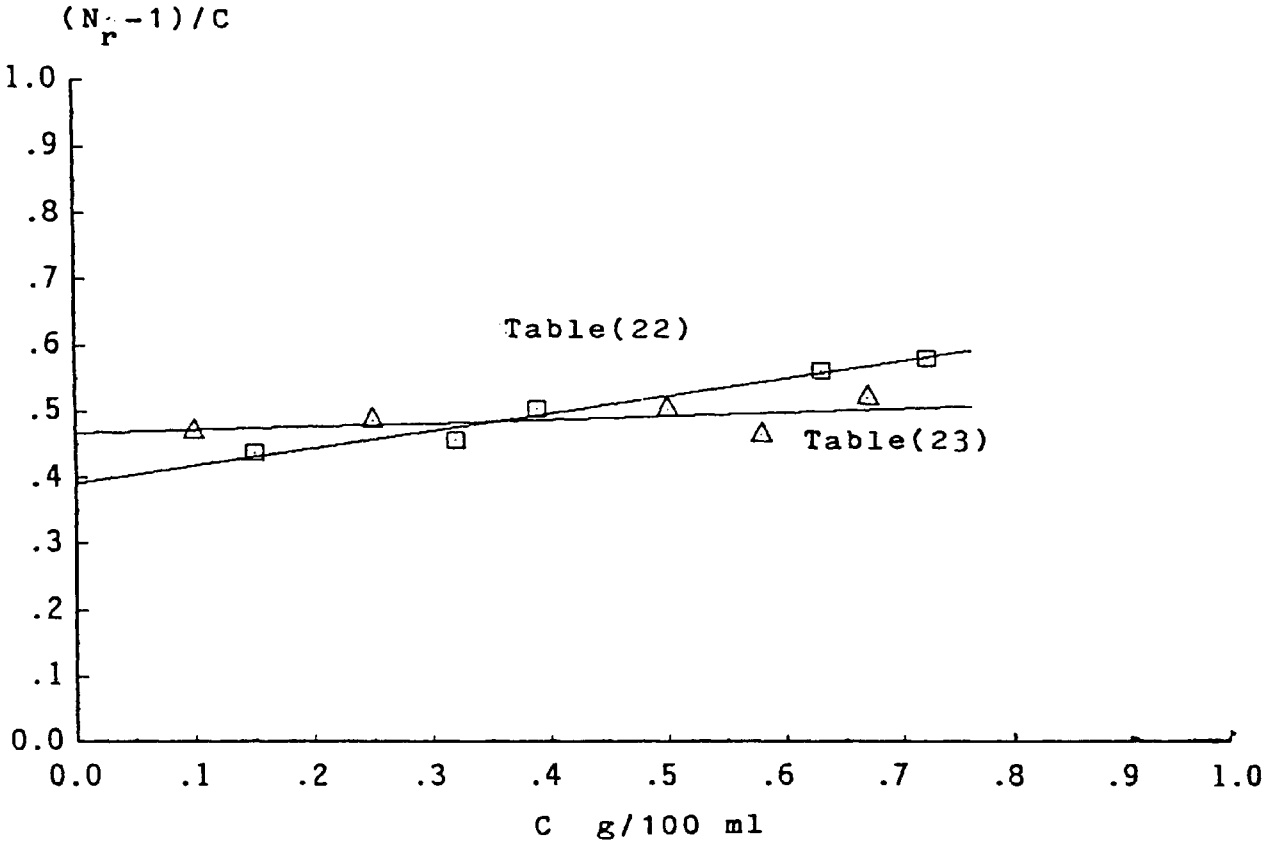
Run	C (g/100ml)	N_r	$\frac{N_r - 1}{C}$
1	0.10	1.0471	0.47
2	0.25	1.1225	0.49
3	0.50	1.2550	0.51
4	0.58	1.2725	0.47
5	0.67	1.3552	0.53

Linear Regression Results (Figure 5)

Slope	0.098
$\frac{N_r - 1}{C}$	0.448
Correlation coefficient	0.716
Standard error	0.026

Figure Number (5)

Graph to determine the I.V. of PET pellet



50% X-ray Film + 50% Virgin PET Blend

Table (24)

Run	C (g/100ml)	N_r	$\frac{N_r - 1}{C}$
1	0.14	1.1162	0.830
2	0.30	1.2625	0.875
3	0.80	1.7000	0.875
4	0.52	1.4992	0.960
5	0.70	1.6825	0.975

Linear Regression Results (Figure 6)

Slope	0.130
$\frac{N_r - 1}{C}$	0.839
Correlation coefficient	0.576
Standard error	0.058

60% X-ray Film + 40% Virgin PET Blend

Table (25)

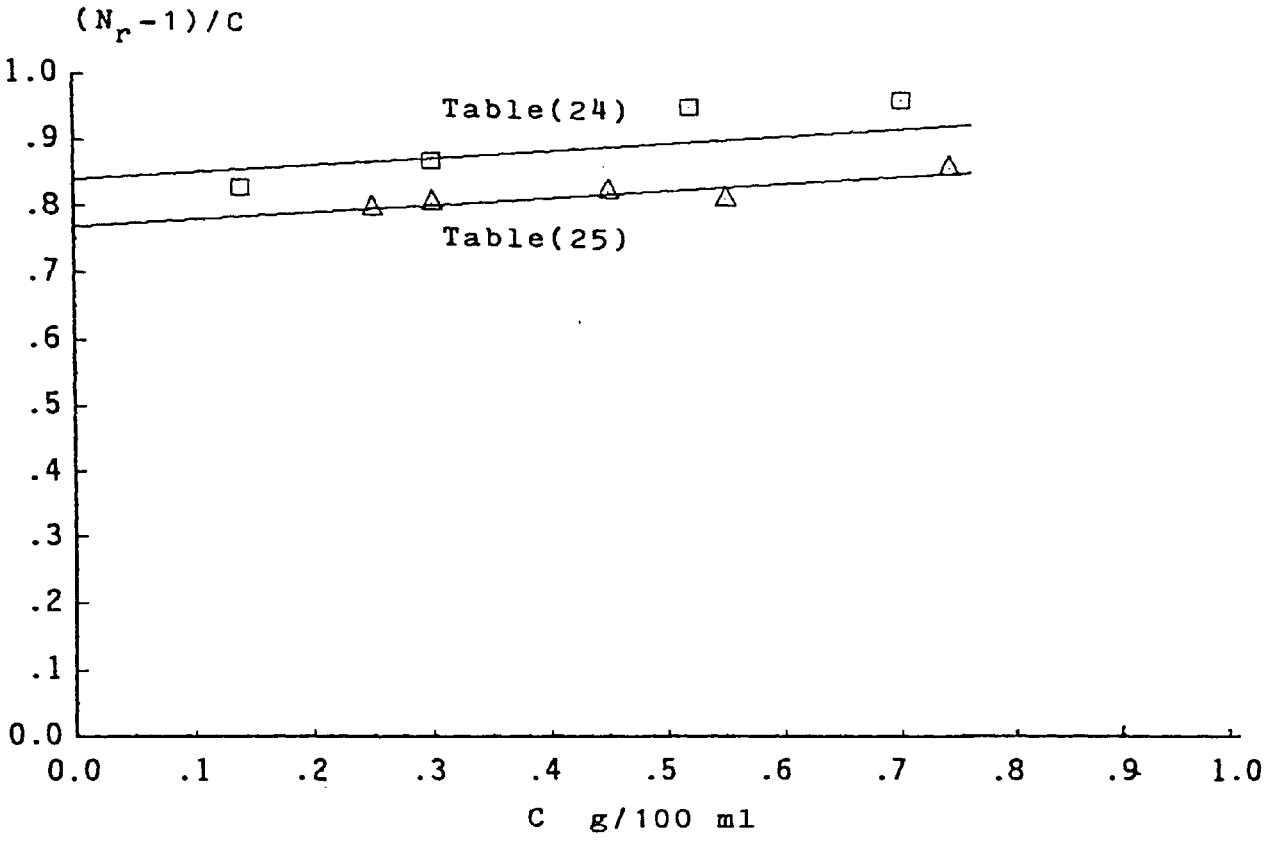
Run	C (g/100ml)	N_r	$\frac{N_r - 1}{C}$
1	0.25	1.2000	0.80
2	0.30	1.2430	0.81
3	0.45	1.3735	0.83
4	0.55	1.5451	0.82
5	0.74	1.6438	0.87

Linear Regression Results (Figure 6)

Slope	0.126
$\frac{N_r - 1}{C}$	0.768
Correlation coefficient	0.925
Standard error	0.012

Figure Number (6)

Graph to determine the I.V. of PET Blend



4.8 **Tensile Strength and Elongation**

Plastics are being increasingly recommended for purposes which involve the withstanding of stresses.

The most important properties are the tensile strength and elongation. To withstand rupture, by pulling apart, is a factor of prime importance when a material is being considered for use as a stress bearing member.

The property of some plastics, which frequently prevents their use for the manufacture of strained members, is their poor ductibility as shown by their comparatively small elongation at break.

Theory

1. Tensile Strength at Break (Nominal)

This can be represented by dividing the load at break by the cross sectional area.

Tensile strength at rupture

$$= \frac{\text{Load at rupture, } P_r}{\text{Cross Sectional Area, A}}$$

$$\sigma r = \frac{P_r}{A}$$

2. Percentage Elongation at Break

This can be represented by dividing the elongation at the moment of rupture of the specimen by initial gauge length of the specimen and multiplying by 100.

$$\text{Percentage elongation, } e\% = \frac{\text{elongation at rupture}}{\text{original length}} \times 100$$

$$e\% = \frac{\text{gauge length - original length}}{\text{original length}} \times 100$$

$$e\% = \frac{L_1 - L}{L} \times 100$$

3. Modulus of Elasticity (Young's Modulus)

It is defined by Hooke's law as the ratio of direct stress σ to strain produced ε and is called Young's Modulus or the Modulus of Elasticity (E).

$$E = \frac{\sigma}{\varepsilon}$$

For bar of uniform cross section A, length l, and p is the load applied, the stretch or elongation produced X

$$E = \frac{pl}{AX}$$

Procedure

A load range was selected such that specimen failure occurs within its upper two thirds. A few runs were tried to select a proper combination of load range and specimen width [33].

The grip was calibrated and balanced to zero and the total length between the grip marks was recorded.

A specimen of known rectangular cross-sectional area was placed between the grips of the testing machine. Care was taken in aligning the long axis of the specimen with the imaginary line joining the points of attachment of the grips to the machine.

Then the grips were tightened evenly and firmly to the degree necessary to minimise slipping of the specimen during the test, then the machine readings were recorded.

Results

Table (26)

Run	Specimen Width (mm)	Specimen Length (mm)	Specimen Area (mm^2)	Elongation %	Tensile Strength N/mm^2	Modulus of Elasticity N/mm^2
A	2.92	10.20	29.78	0.67	0.77	232.79
B	2.91	10.12	29.45	0.67	0.78	252.25
C	2.89	10.21	29.51	0.48	1.57	227.39
D	2.89	10.14	29.41	0.87	0.93	228.17
E	2.90	10.11	29.32	0.77	1.19	253.37
F	2.92	10.11	29.52	0.63	0.55	220.18
G	2.89	10.13	29.28	0.58	1.14	253.75
H	2.89	10.08	29.13	0.77	1.14	238.00

The table number 27 shows the blending results of PET from X-ray film plus Virgin PET manufactured by I.C.I., commercially known as Melinar, which has the following specifications:-

Tensile strength = 3.68 N/mm^2

Density = 1410 kg/m^3 at 25 ^oC

I.V. = 0.92

% of water absorption = 0.60%

Table (27)

Specimen	Percentage Elongation	Tensile Strength N/mm^2	Blending Temperature for 2 hours ^oC
1	380	1.50	270
2	360	1.55	275
3	490	1.53	280

Specimen 1and 2

Blens of 60:40% film:virgin PET

Specimen 3

Blend of 50:50% film:virgin PET

CHAPTER FIVE

Discussion of Results and Conclusions

The experimental results in Chapter 4, show that the silver content in used X-ray film and unexposed X-ray film depends upon the age of the X-ray and the intensity of light exposure. Figure No. (1) year of manufacturing of X-ray vs the percentage of silver in the film, shows that the silver content in X-ray film manufactured in the 80's is almost half of that manufactured in the 50's. Also from the results in Table 8 that the X-ray plates manufactured in the 1950's and 60's are not the same density as those manufactured in the 70's and 80's. This is because the material used in the 50's and 60's was cellulose triacetate (CTA), and the material used in the 70's and 80's is poly (ethylene terephthalate) PET, as it was confirmed by the Infra-red Reflectance (ATR), Figure Nos. (2) and (3).

Table 10 shows that the content of adhesive tape is 1.5% and the loose paper is 7%.

Experiments in Section 4.4 show that PET is hydrophobic i.e. it is difficult to wet it with water and the results in Table 11 show that the moisture content of PET increases with time of exposure to the atmosphere. The percentage of water absorbed depends to some extent on the shape of the test sample, as shown in Tables 11-13.

The moisture content of the PET film is related to the mechanical strength and appearance. The effect upon these properties, of change in moisture content, depends largely on the type of exposure (immersion in water or exposure to high humidity) and duration of the exposure. As it was expected the coated film absorbed much less water than de-silvered and delaminated samples, because the former is coated with silver emulsion layers which act as a barrier. So before the pelletisation process, the PET flakes were dried in a dehumidifying drier, capable of circulating a continuous supply of warm air to the pellets at the recommended controlled temperature of 200°C. Blended X-ray pellets with virgin PET also required drying. Care was taken during the drying operations not to exceed a temperature of 200°C because the PET melts at 220°C.

Moisture is a vital factor, and the presence of it in the PET will have a negative influence on the surface appearance, strength and physical properties as shown from the results in Section 4.8 and 4.7. The viscosity of PET was affected drastically by the moisture content of the sample.

The results of I.V. tests were initially affected by the deep blue colouration. To obtain a clear solution, the sample of X-ray film was dissolved in a solution of o-chlorophenol at room temperature, while the pellet samples had to be warmed up to 80°C, for three days. Moisture content studies by drying the film flakes and pellets to constant weight, shows

that the film flakes absorbed 0.55% water and the pellets absorbed 0.0348% water. For the period of 30 days exposure, Table 14, this is due to the larger surface area of the flakes exposed to the atmosphere dried under the same conditions, and the following I.V. results were obtained.

Table (28)

	PET Film	PET Pellets
Dry	0.738	0.448
Moist	0.589	0.391
% increase after drying	20.19%	12.72%

The results in Table 28 confirm that the moisture content depresses the intrinsic viscosity of the PET in both PET film and PET pellets. The possible error that could have happened in these results is if the film samples were not representative of the bulk stock.

In addition, extrusion of moist PET will give substantial breakdown of the PET, as it can be seen from the pelletisation of PET X-ray flakes that the I.V. decreased from 0.738 to 0.448. This may be caused when the PET melted to form pellets, air reacts rapidly with it and as a result the air gets trapped in the pellets. This may also explain the reduction in the I.V. of the pellet form. The I.V. of 0.738 of dried PET is a satisfactory result, therefore venturing into the costly build up of I.V. by the Zimmer

reactors may not be required (Zimmer reactors are used to increase the I.V. by heating the polymer to 200°C and cool it under nitrogen blanket).

PVDC can be dissolved away from the PET film flake substrate using a number of solvents, which were proven very satisfactory as shown in Table 15, but this method suffers from toxicity or flammability problems.

Cyclohexanone, chlorobenzene, and 1.4 dioxane all suffer from hazard problems. A more fundamental problem is that spreading of solutions onto previously uncoated surfaces can leave the PET flakes with PVDC coated in areas not originally coated.

A process using chlorinated solvents does suffer from major problems of absorption of the chloro-carbons into the PET flakes, although it is acceptable for water removal prior to injection moulding. It may be less acceptable due to the effect of chloro-fluro Carbon on the environment. This could be construed as an unacceptable method for solving another environmental problem. It is also shown that the critical steps in delamination and removal of PVDC and adhesive papers is to ensure that the feed X-ray film is cut in a manner so that the chips have a creased cut shape, so that they do not seal each other.

Table 15 shows that hammer cut is more effective than the

knife cut. Table 16 shows the economic condition, for the penetration of the solution to take place at the interface between the solution and the PET substrate. When the temperature is 60^{o}C and sodium hydroxide concentration is 1.0 g/l then coatings loosen and soften. The segregation of PET was carried out by the flotation process in water media containing a wetting agent at room temperature, with continuous air agitation.

PVDC flakes and adhesive tapes float to the top while the PET flakes, sink to the bottom. This action took place because when a very small quantity of wetting agent was added to the water, the surface tension of the water was reduced and the PVDC changed from being hydrophobic to hydrophilic.

On the other hand, the drop in the temperature of the media causes the PVDC layer to shrink and its shrinking rate is different from that of the PET layer, and hence the separation of the two polymers.

The segregation step may require a multi-stage approach as the PET can act as an excellent filter bed for the removal of PVDC and any other contaminants. The results of the PVDC test shown in the Table 16, indicate that PVDC content in the unexposed film was 2.7% and green film shows heavy contamination due to the presence of PVDC and photographic salts. After de-silvering the flakes, the result shows in Table 17, that the PVDC content was reduced to nearly half

that of the green film and the remaining PVDC left on the film must have come from the second layer. Table 19 shows that no PVDC nor photographic salts were left after using the process in (4.5). That means that the PET is suitable for extrusion, but the mechanical test, confirmed that the PET was unsuitable. The test results in Table 26 shows that the elongation percentage is 0.63 to 0.87 and tensile strength 0.58 to 1.57 N/mm^2 for the de-silvered/delaminated X-ray film.

In this case the test shows that the tensile strength may be sufficient, but the elongation percentage is very low, for this material to be extruded.

For this reason the material was blended with the virgin PET (Melinex). The results of the blending show in Table 25 that a blend of 60% X-ray film and 40% of virgin PET produced an IV of 0.768, and a blend of 50:50% produced an IV of 0.839.

Also the results in Table 27 show the elongation percentage of 60:40% blend produced 360% while 50:50% blend Table 27 produced 490%. So in this way the material can be used and recycled as marketable pellets.

The results of the following blends are not available as it takes more time to be completed.

Table (29)

Batch Number 1	Weight (kg)
Clean X-ray film	50
Clean Lithographic film	50
Clean bottle chip	50

Batch Number 2	Weight (kg)
Clean X-ray film	25
Clean Lithographic film	28
Clean Cellulose film	25
Clean bottle chip	25

Batch Number 3	Weight (kg)
Blend 50/50 mix	
X-ray film and bottle	50
Lithographic film and bottle	50
X-ray film and lithographic film	50

Costing of the process cannot be enclosed in this work due to the company regulations.

CHAPTER SIX

Mass Balance and Heat Requirements

6.1 Mass Balance Across the Plant

6.2 Heat Requirements

6.1 Mass Balance Across the Plant

The analytical results quoted in Tables 7, 9, 10 and 17 were used as the basis for the calculations of mass balance (see the flow sheet in Chapter 8). The raw material consists of the following compounds:

Table (30)

Compound	% Wt
Film	93
Loose paper	7

The film consists of the following compounds:

Compound	% Wt
Silver	1.20
PVDC	2.00
Adhesive tape	1.50
Gelatin	0.30
PET	95.00
	100.00

Basis 1000,000 kg starting raw material per year. Then the input rate of raw material = 417 kg/hr

See flow sheet Appendix B, page110 .

Table (31)

Paper/Film Classifer

Component	Stream (kg/hr)		
	3	1	2
Raw material	417		
Loose paper		29.19	
Film			387.81

Table (32)

Leaching Reactor (T1)

Component	Stream (kg/hr)		
	2	4	5
Film	387.81		
Silver		4.65	
PVDC		3.88	3.88
Adhesive tape		1.16	4.66
Gelatin		1.16	
PET	_____	____	368.42
	387.81	10.85	376.96

T1 - Gelatin Filter Unit

In this unit the following components are removed:

All gelatin

50% of the PVDC

20% of the adhesive tape

Table (33)

Component	Stream (kg/hr)		
	4	6	7
Silver	4.65	4.65	
PVDC	3.88		3.88
Adhesive tape	1.16		1.16
Gelatin	1.16	____	1.16
	10.85	4.65	6.20

Table (34)

Silver Recovery Unit

All silver recovered in this unit

Stream 8 4.65 kg/hr

Table (35)

Hot Tank (T2)

Component	Stream (kg/hr)		
	5	9	10
PVDC	4.65	0.39	4.26
Adhesive tape	4.66	4.20	0.46
PET	368.42	____	368.42
	377.73	4.59	373.14

Table (36)

T2-Filter Unit

Component	Stream (kg/hr)	
	9	11
PVDC	0.39	0.39
Adhesive tape	4.20	4.20
	4.59	4.59

Table (37)

Cold Tank (T3)

Component	Stream (kg/hr)		
	10	12	13
PVDC	4.26	4.26	
Adhesive tape	0.46	0.46	
PET	368.42	____	368.42
	373.14	4.72	368.42

T3-Filter Unit

All PVDC and adhesive tape are removed in this unit stream 14.

6.2 Design of Reactor and Heat Requirements

6.2.1 Construction of the Steam Jacket

The steam jacket covers the domed end of the tank and four fifths of the cylindrical portion. Its diameter will be 18 cm greater than the tank. The same materials used to construct the tank shell are used for the construction of the jacket, mild steel 2 cm thick, lined with 0.28 cm type 304 stainless steel on the inside. This includes a corrosion allowance of mild steel on the outside.

The total thickness of the jacket material = 2.28 cm.

6.2.2 Dimensions of the Reactor

Volume of solution	=	9.0 m^3
Volume of reactor	=	13.5 m^3
Diameter of reactor	=	2.4 m
Diameter of hemispherical end	=	2.4 m
Length of cylindrical section	=	3.05 m
Thickness of reactor wall	=	12.7×10^{-3} m

Volume of solution in hemispherical end

$$= \frac{4 \pi r^3}{3 \times 2}$$

$$= \frac{4 \times \pi \times 1.2^3}{6}$$

$$= 3.62 \ m^3$$

Therefore volume of solution in cylindrical section

$= 9 - 3.62 = 5.38\ m^3$

using $V = \pi r^2 h$

Then height of solution in cylindrical section, h

$$= \frac{V}{\pi r^2}$$

$$h = \frac{5.38}{\pi \times 1.2^2} = 1.9\ m$$

6.2.3 Agitator Design

A standard tank configuration, which provides adequate mixing for most requirements, has the following geometrical relationships [34].

1. The agitator is a six blade, flat blade turbine impeller.
2. The impeller diameter is one third of the tank diameter.
3. The height of the impeller from the tank bottom is equal to the impeller diameter.
4. Impeller blade width is one fifth of the impeller diameter.
5. The impeller blade length is one eighth of the impeller diameter.
6. Four baffles, vertically mounted on the tank wall, are employed extending above the liquid surface.

7. The baffle width is one tenth of the tank diameter.

As baffles are employed the agitator will be mounted along the centre line of the vessel. The dimensions of the mixer will be as follows:-

Agitator type	0.800 m
Impeller diameter	0.800 m
Height of impeller from bottom of tank	0.800 m
Each impeller blade width	0.160 m
Each impeller blade length	0.100 m
Number of baffles	4
Baffle width	0.24 m
Impeller speed	1.25 rev/s

From [34] the number of turbines to be used on a shaft is given by Weber's formula

$$\text{Number of turbines} = \frac{\text{WELH}}{\text{Tank diameter}}$$

where WELH = water equivalent of liquid height

$$\text{Number of turbines} = \frac{3.6}{2.2} = 1.7$$

Number of Turbines to be used = 2

These are placed one impeller diameter apart (0.800 m) to prevent the formation of unagitated areas.

6.2.4 Heat Transfer Area

A_i = Inside heat transfer area = $(\pi \times D_i \times L) + \frac{\pi D_i^2}{4}$

where

D_i = Internal diameter = 2.4 m

L = Height of liquid in cylindrical section = 1.9 m

$$A_i = (\pi \times 2.4 \times 1.9) + \frac{\pi \times 2.4^2}{4}$$

$$A_i = 18.86 \text{ m}^2$$

Similarly,

A_o = Outside heat transfer area = $\pi D_o L + \frac{\pi D_o^2}{4}$

where

D_o = Outside diameter of reactor = 2.4254 m

$$A_o = (\pi \times 2.4254 \times 1.9) + \frac{\pi \times 2.4254^2}{4}$$

$$A_o = 19.11 \text{ m}^2$$

Mean heat transfer area = 18.98 m^2

6.2.5 Jacket Side Heat Transfer Coefficient

The following equation applied to a vapour condensing on a vertical tube [35].

$$h_o\left(\frac{\mu_f^2}{K_f^3 \, e_f^2 \, g}\right)^{1/3} = 1.47\left(\frac{4G'}{\mu_f}\right)^{-1/3}$$

where

h_o = Outside heat transfer coefficient

μ_f = Viscosity of condensing vapour

K_f = Thermal conductivity of condensing vapour

e_f = Density of condensing vapour

G' = Mass flow rate/linear metre.

and μ_f, K_f and e_f are evaluated at temperature t_f, the condensing film temperature.

$t_f = \frac{1}{2} (T_v - t_w)$

where

T_v = Condensing vapour temperature

t_w = Wall temperature.

T_v is constant at constant pressure, but t_w will vary with the bulk liquid temperature.

If it is assumed that steam is available at 15 p.s.i.g. and at a flow rate of 0.1 x 10 kg/sec, then from steam tables [36] the value of T_v will be 120 ^oC.

Assuming the temperature of the solution will drop to 50^oC when the new batch of film is transferred to the reactor then t_w will vary from 50^oC to 95^oC.

Therefore, $t_f(i)$ = 85^oC and $t_f(f)$ = 107 ^oC.

Taking t_f as the mean i.e. 96.25^oC and using values for condensed steam at this temperature from [38] for μ_f, K_f

and e_f.

$\mu_f = 0.235 \times 10^{-3}$ kg/ms

$e_f = 962$ kg/m^3

$K_f = 0.674$ W/m^2(^oC/m)

$G' = 0.1 \times 10$ kg/s

Therefore

$$G' = \frac{1.0}{\pi D} = \frac{\text{Mass Flowrate}}{\text{Circumference}} = \frac{1}{\pi \times 2.4254}$$

$G' = 0.131$ kg/ms

Therefore

$$h_o\left(\frac{(0.235)^2 \times 10^{-6}}{(0.674)^3 \times (962)^2 \times 9.81}\right)^{1/3} = 1.47\left(\frac{4 \times 0.131}{0.235 \times 10^{-3}}\right)^{-1/3}$$

h_o = Heat transfer coefficient for condensing steam

= 4154 Wm^{-2} ^oC

6.2.6 Inside Heat Transfer Coefficient

As the solution is mainly water the values for density, thermal conductivity and specific heat of water are taken as those for the solution as a whole. As these values are fairly constant over the temperature range considered [36] the arithmetic mean is taken in each case.

The values for these constants are:

C_p = Thermal capacity = 4.2 kJ/kg K

p = Density = 975 kg/m^3

μ = Viscosity = 0.038 kg/ms

K = Thermal conductivity = 0.652 W/m^2(^{o}C/m)

Brooks and Su[37] have developed the following equation for jacketed reactors where the Reynolds number is greater than 400.

$$\frac{h_i D_t}{K} = 0.74\ (Re)^{0.67}(Pr)^{0.33}\left(\frac{\mu_w}{\mu}\right)^{-0.14}$$

(N.B. At the low temperature range used $\left(\frac{\mu_w}{\mu}\right)$ is approximately one).

where

h_i = Inside heat transfer coefficient (Wm^{-2} ^{o}C^{-1})

D_t = Diameter of tank (m)

Re = Reynolds number for mixing

Pr = Prandtl number

As $Re = \frac{PNDa^2}{\mu_w}$

where

N = Impeller speed (rev.s^{-1}) = 1.25 s^{-1}

Da = Diameter of impeller (m) = 0.800 m

μ_w = Viscosity at wall temperature = 0.038 kg/ms

Then

$$Re = \frac{962 \times 1.25 \times (0.800)^2}{0.038}$$

$$Re = 20253$$

$$Pr = \frac{C_p \mu}{K}$$

Therefore

$$\frac{h_i \times 2.4}{0.652} = 0.74 \times (20253)^{2/3} \times \left(\frac{4.2 \times 10^3 \times 0.038}{0.652}\right)^{1/3}$$

$$h_i = 934 \ Wm^{-2} \ {}^oC^{-1}$$

Inside heat transfer coefficient = 934 Wm^{-2} $^oC^{-1}$

6.2.7 Overall Heat Transfer Coefficient

There are four resistances to heat transfer.

1. Inside film (water side) = $1/h_i$.
2. Reactor wall = $1/K$.
3. Outside film (jacket side) = $1/h_o$.
4. Scale and dirt on reactor wall = R_d.

$$\frac{1}{UA} = \frac{1}{h_i A_i} + \frac{1}{K A_m} + \frac{1}{h_o A_o} + \frac{R_d}{A_m}$$

where

K = Thermal conductivity of reactor wall

l = Thickness of reactor wall

A_m = Logarithmic mean area of heat transfer

U = Overall heat transfer coefficient per m^2

$\frac{1}{U}$ = Overall resistance to heat transfer per m^2

As $\frac{A_i}{A_o} = \frac{A_m}{A_o} = 1.0$

Therefore

$$\frac{1}{U} = \frac{1}{h_i} + \frac{l}{K} + \frac{1}{h_o} + R_d$$

Now

$l = 12.7 \times 10^{-3}$ m

$K = 48.5$ $Wm^{-2}(^oC/m)$ (37)

From Kern[35] Rd may be taken as 0.88×10^{-3} m^2 $^oC/W$

Therefore

$$\frac{1}{U} = \frac{1}{934} + \frac{1}{4154} + \frac{12.7 \times 10^{-3}}{48.5} + 0.88 \times 10^{-3}$$

$U = 406.3$ Wm^{-2} $^oC^{-1}$

Overall heat transfer coefficient including scale resistance = 406.3 Wm^{-2} $^oC^{-1}$

6.2.8 Heating Time

In an agitated vessel containing Mkg of liquid with specific heat Cp and initial temperature t, heated by a condensing medium of constant temperature Ts, the batch temperature at any given time θ is given by the differential balance [35].

$$dQ = MC_p \frac{dt}{d\theta}$$

where

dQ = Heat transferred/unit time

and

$dQ = UA\ (T_s - t)$

therefore

$$\frac{dt}{dQ} = \frac{UA}{MC_p}\ (T_s - t)$$

where

U = Overall heat transfer coefficient

A = Heat transfer area

On integration this becomes

$$\ln \frac{T_s - t_1}{T_s - t_2} = \frac{UA}{MC_p} \times \theta$$

where θ is the time required in seconds to heat the liquid from the initial temperature t_1 to the final temperature t_2.

$T_s = 120\ ^oC$

$t_2 = 95\ ^oC$

$t_1 = 50\ ^oC$

$U = 406.3\ Wm^{-2}\ ^oC^{-1}$

$A = 18.98\ m^2$

$C_p = 4.2 \times 10^3\ JKg^{-1}\ K^{-1}$

$M = 9.0 \times 975 = 8775\ kg$

Therefore

$$\ln\left(\frac{120 - 50}{120 - 95}\right) = \frac{406.3 \times 18.98}{8775 \times 4.2 \times 10^3} \times \Theta$$

Θ = 1 hour 22 mins

Time required to heat batch of solution containing one tonne of film from 50°C to 95°C is 1 hour 22 mins.

CHAPTER SEVEN

Management and Recycling

7.1 Introduction

7.2 Marketing and Economy

7.3 Usage of PET

7.1 Introduction

The European Commission made it clear [38] the energy recycling of plastic by incineration is not a preferred option, and strongly believe in plastic recycling as the solution to waste treatment.

Thermal recycling of plastic is a solution for waste management, but it should be limited to that fraction of plastic waste which may not be recycled by chemical or physico-mechanical treatment.

The European Community [39] plans to promote the favoured option of plastic recycling, these include:

1. Substantial VAT reductions for recycled products.
2. Reserving public contracts entirely for recycled products.
3. Establishing of information centres dealing with availability of plastic wastes.
4. Organising financial assistance for research and development of plastic recycling technology.

Waste Management strategy is based on three principles:

1. Waste prevention in plastic, means recycling or changing the surface coating of the plastic and clean technology.
2. Increase of recycling.
3. Safe disposal.

7.2 **Marketing and Economy**

PET is a significant influence and one of the most popular plastics in the world for several reasons:

A. The reason behind the increase in this material is that a good oxygen and carbon dioxide barrier, of around 0.5 $cc/m^2/24$ hrs is obtained i.e. the market moved to replace the 12 ounce aluminium cans with PET cans. The barrier coating used is Saran Polymer (PVDC).

The difficulty of removing Saran makes PET film difficult to recycle.

B. Changes in lifestyle in recent years have also boosted PET film demand. The key factor behind this is the development and more importantly growth of microwave ovens.

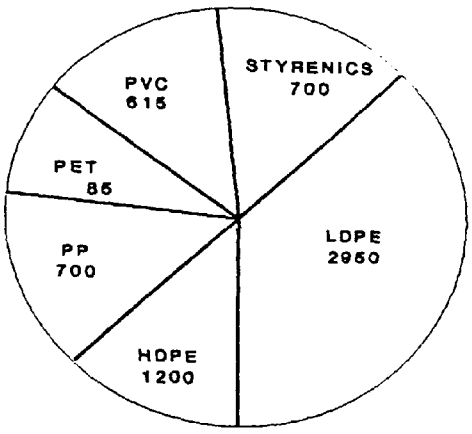
European consumption of PET in microwave ovens is growing fast at about 200 tonnes a year [39].

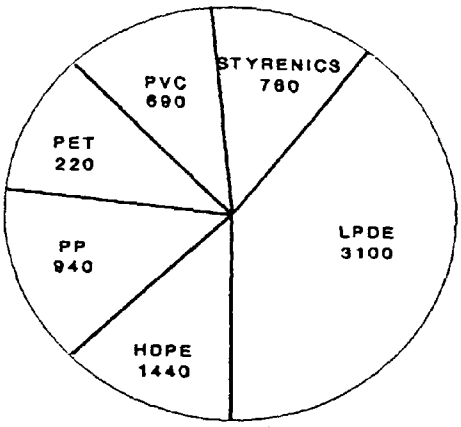
C. One of the most popular products in the construction industry is for spun bond road matting furnished by the textile industry. The material is made from poly (ethylene terephthalate) PET.

D. PET film, offers a good barrier to both oxygen and water, highly resistant to heat, chemicals and ultra violet rays. This has increased its share of the European packaging

market.

Figure Number (7)





Total: 6250 kT

1984

Total: 7150 kT

1990

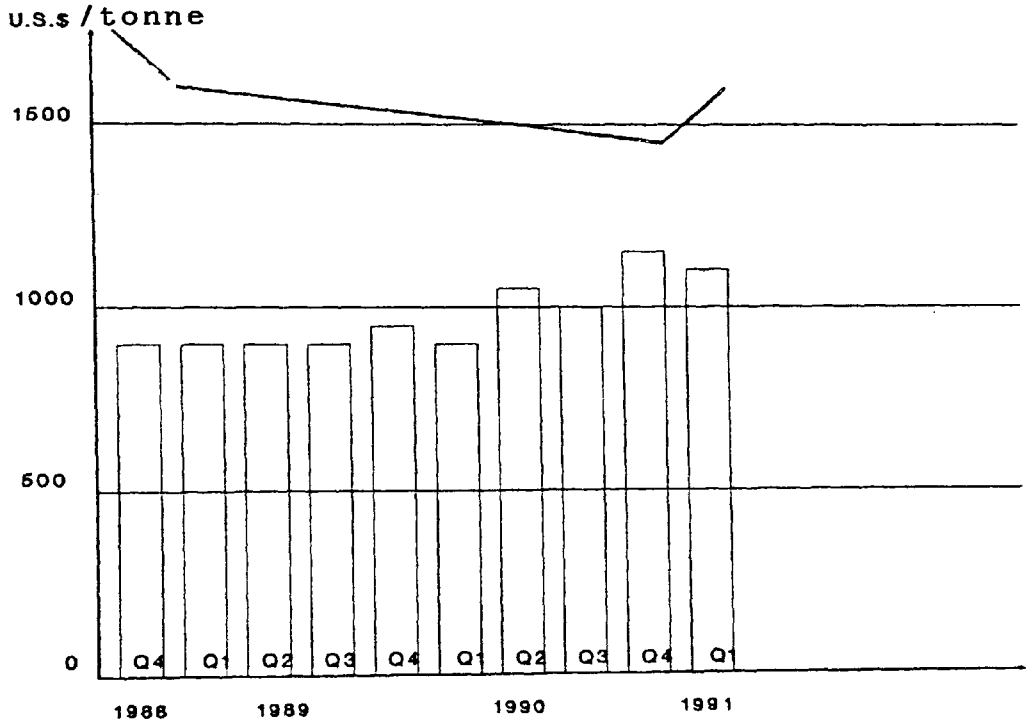
Plastics consumption in packaging, West Europe [40]

Around 3.1% of the total market in 1990 involved PET compared with 1.4% in 1984.

At the current time the virgin PET market has moved into a depressed state in the first quarter of 1989. This may be due to:-

1. A large volume of PET is being recycled to industry, and
2. Incineration of plastic is being limited.

Figure Number (8)



W. European PET price vs cost (40)

——— PET price ▭ PET production cost

The price situation may be difficult to understand when viewed against the volume demand side of the market depending on the weather conditions in Europe (i.e. The warmer the weather the higher the demand, resulting in higher PET prices).

Industry sources expect there will be continued upward pressure on production of virgin PET in the ninety's and it is anticipated that this could lead to an increase in demand for the recycled PET, from bottle and film sources. This demand will come from companies engaged in the manufacturing of polyester fibres, carpets, packaging material, industrial strapping, show fence, non-woven textiles and construction material. Manufacturers using PET are currently paying £1.20 per kilo for virgin material and about £0.50 per kilo for recycled PET bottle material. The PET recycled from film will be priced at £0.40 per kilo, which makes it a competitive commodity.

There are many benefits in recycling:

A. Provides available alternative and accessible raw materials.

B. Reduces imports of primary raw materials and finished products, and increases exports both of which have a beneficial effect on the balance of payments.

C. Reduces the solid waste disposal problems and protects

our environment from salvageable waste, which would otherwise go to landfill or incineration.

D. Reduces the waste of our natural wealth.

E. Saves energy.

F. Contributes to the conservation of the environment for present and future generations.

7.3 **Usage of PET**

Typical usage area for pure/recycled PET with acceptable viscosities:

A. Electrical outlets include:

1. Slot liners for electrical motors.
2. Wire and cable insulation.
3. Transformer insulation.
4. Capacitors.
5. Printed and laminated circuitry.

B. Variable outlets include:

6. Magnetic recording tapes.
7. Magnetic memory cards.
8. Microphone diaphragms and loudspeakers.
9. Typewriter ribbons.
10. Computer tapes.
11. Pressure - sensitive tapes.
12. Metallic yarn.

13. Decorative laminates on automobiles.
14. Echo satellite balloons.
15. Missile diaphragms.
16. Very light aircraft.
17. Glazing applications.
18. Industrial belting.
19. Book jackets.
20. Apparel stays.
21. Roll leaf application.
22. Acoustic tiles.
23. Spring roll shelving.
24. Ticker tape.
25. Pipe wrap.
26. Photographic film base.
27. Packaging.
28. Boil-in-the-bag food application.
29. Heat - shrinkable wrappings.
30. Window coating.
31. Formable packages.
32. Plastic bottles.
33. Engineering reproduction.
34. Graphic art film.
35. Decals.

CHAPTER EIGHT

Description of a Recommended Plant and Control

8.1 **Description of a Recommended Plant**

8.2 **Instrumentation and Control of Plant**

8.1 Description of a Recommended Plant

The recommended recovery plant of PET from used X-ray film illustrated in (Figure 9) comprises a pulveriser where the film and paper is shredded to small particles; a hammer mill is chosen for this type of duty. The particle size of material leaving the mill is of the order of magnitude 10 - 25 mm. The pulverised paper and X-ray film mixture is transported via a paddle blower through a vertical ducting pipe 300mm diameter and 4m high [3] where the heavy material, mainly consisting of metals, glass and stones are separated from the paper/film mix.

The paper/film mix is then directed to an air classifier where the light loose paper fraction is separated from the film. The material is then transported to a reactor (T1) where the silver in the X-ray film is leached out using alkaline cyanide solution and the silver recovered at the cathodes of the electrolysis cells. The gelatin compound is recovered at this stage using a filter press installed with the same cycle. A neutralisation unit is needed to neutralise the cyanide on the surface of the film using sodium hypochlorite solution.

The material is then blown to the hot reactor (T2) containing wetting agent in alkali solution controlled to pH of 10 - 11. The temperature of the reactor (T2) is raised to 95 ^{o}C, the agitation is provided by flat turbine impellers. At this stage almost all PVDC and loose adhesive tapes are separated

from the PET.

Then the material is transported by a blower to a washing tank (T3) controlled to pH of 6 - 8 using dilute sulphuric acid at a temperature of 15 - 25 ^{o}C. Air at 1350 kN/m^2 is introduced at the bottom of the tank through spargers to maintain uniform agitation and provide a lift off of the small particles of flaked PVDC and the adhesive loose tape at the top of the tank and then recovered by filtration.

The PET is conveyed to a continuous centrifuge system to extract most of the surface moisture, and then transported to a dryer. The resulting clean blue coloured PET is blended 50:50 with virgin PET in a hopper blender. The blended product fed to a double screw pelletiser and then packed in bags using a vacuum packer.

See the flow sheet in Appendix B, page 110..

8.2 Instrumentation and Control of Plant

As can be seen from the flowsheet, three controllers are required.

Temperature Controller

This controls the reactor temperature and will be a simple proportional flow controller which will record the temperature and operate the cooling water and steam valves as necessary to maintain the temperature at 95 ^{o}C.

In case of a failure in the controller system the reactor should also have temperature recorder with an alarm signal on the control panel designed to operate if the reactor temperature goes too high or low during reaction. In this event the valves would be operated manually. In addition, a manually operated valve on a by-pass line over the inlet/outlet valve could be installed in case of valve failure.

pH Controller

The requirement of this controller is to adjust the set point of the sodium hydroxide input controller to pH of 10 -11 in (T2). Also to reduce the pH of the solution in (T3) to pH of 6 - 7.

Therefore, the controller and valves must give a system which has little steady state error, but it is unnecessary to have a system with a fast response. The most suitable type of

controller would be a two term type (proportional and integral) together with a pH indicator on the control panel.

Level Controller

Ultrasonic level sensor is chosen for this requirement, because one resulting measurement of the level is unaffected by vibration which is caused by the operation of the pulveriser.

Two sensors are required in each tank, one for the upper liquid interface level and the second for the lower liquid interface level.

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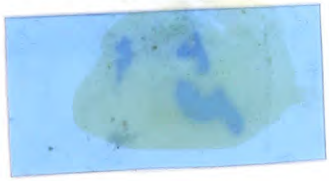
Appendix A

*Large Exposure : x-ray film where 70% of the silver in the plate has been leached out during the developing process.

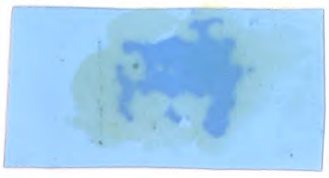
* Low Exposure : x- ray film where 40% of the silver in the plate has been leached out during the developing process.

*Green : Unexposed (unused) x- ray film.

*Total Exposure : X- ray film where all the silver in the plate has been leached out.

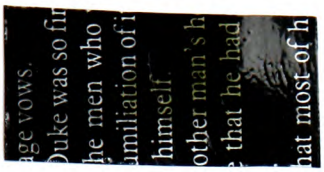


*Clean film : De-silver/de-laminated x-ray film.

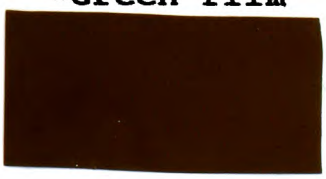


Appendix A (cont..)

Exposed film : Lithographic film where 40% of the silver in the plate has been leached out during the developing process.



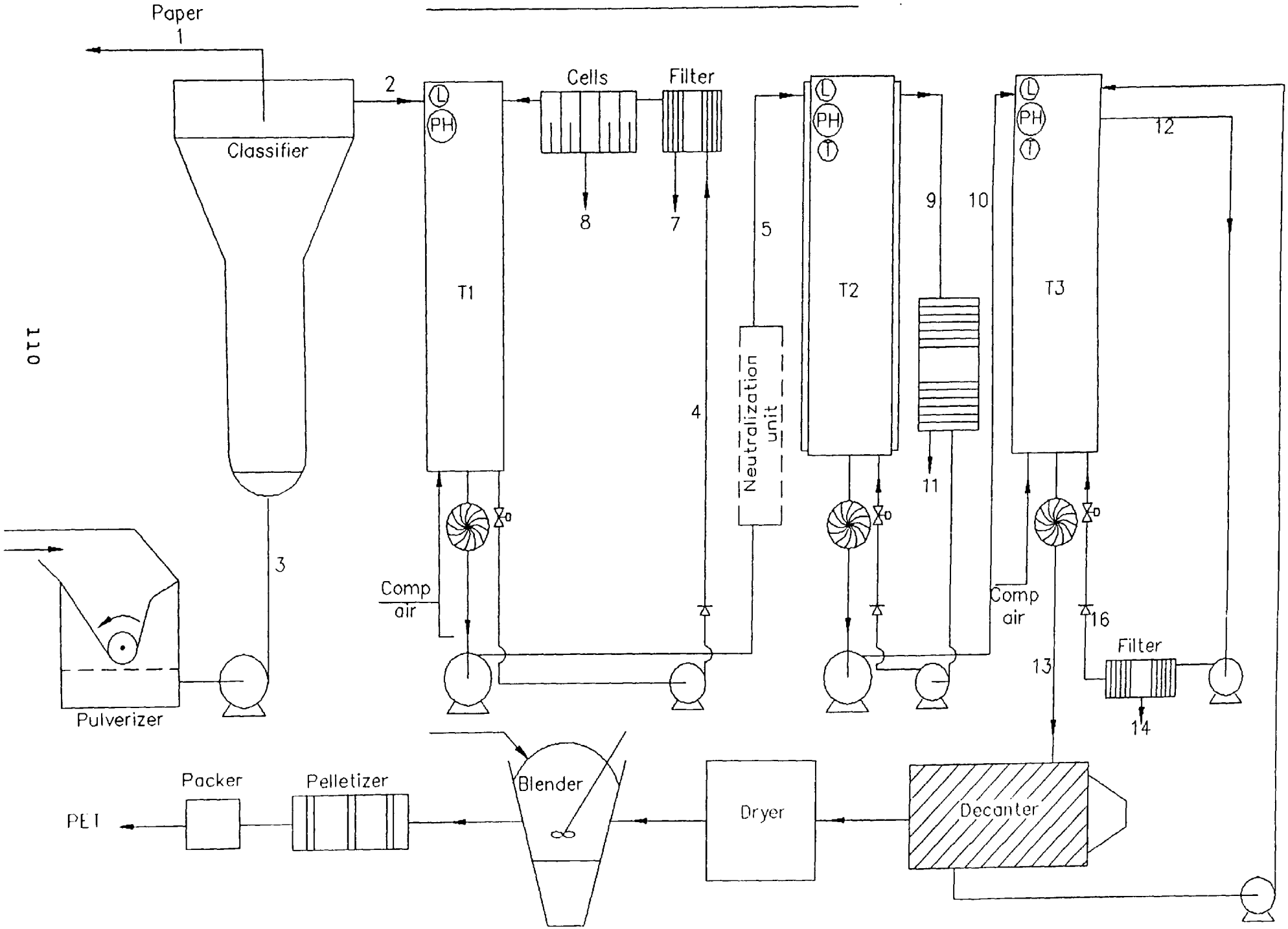
***Green film** : Unexposed (unused) lithogaphic film.



***clean film** : De-silver/de-laminated lithogaphic film.

Pure silver : 99.9% silver ingots.

RECOMMENDED FLOW SHEET (APPENDIX B)



Nomenclature list

A	Cross sectional area
A_i	Inside heat transfer area
A_o	Outside heat transfer area
C	Polymer concentration
C_p	Thermal capacity
EG	Ethylene Glycol
E	Young s modulus
e%	Percentage elongation
e_f	Density of condensing vapour
G	Mass flow rate
h	Hight of solution
h_o	Outside heat transfer coefficient
IV	Intrinsic viscosity
K_f	Thermal conductivity of condensing vapour
L	Original length
L_1	Gauge length
N_r	Relative viscosity
N_s	Solution viscosity
N_{so}	Solvent viscosity
N_{sp}	Specific viscosity
P_r	Load at rupture
T_v	Condensing vapour temperature
t_w	Wall temperature
U	Overall heat transfer coefficient
V	Volume of solution
X	Elongation
μ_f	Viscosity of condensing vapour
ε	Strain
σ_r	Tensile strength at rupture